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PRODUCTION • FABRICATION • TREATMENT • APPLICATION

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Pack up Your Troubles

DID you ever stop to figure why we keep emphasizing the fact that subsidiaries of the United States Steel Corporation employ more than 1700 steel technicians, chemists, metallurgists, research engineers? Why we keep 89 research laboratories constantly at work checking, testing and experimenting? Why in our plants alloy steel production and alloy steel sales have been completely segregated from the commercial steel divisions?

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This vast organization within an organization—these special research, production and sales facilities are geared up to one idea. To give you, the user, the exact grade of steel that will do the best job for you at lowest cost—and to give you that steel in any quantity when you want it and as often as your orders call for.

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Teaching Metallurgy in the High School

by Wesley E. McArdell and Fred P. Peters

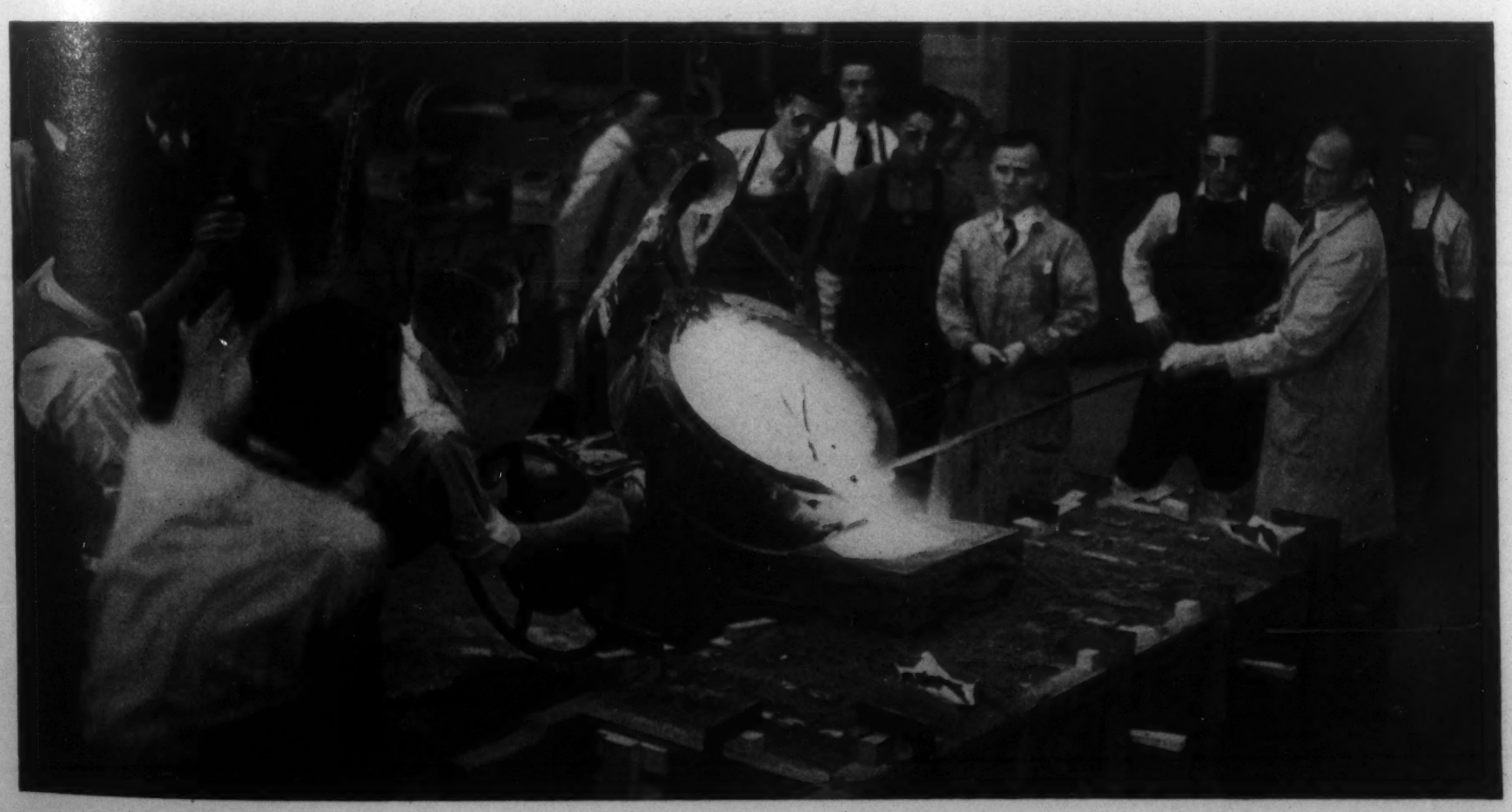
Instructor, Brooklyn Technical High School, Brooklyn, N. Y., and Assistant Editor, METALS AND ALLOYS, *Respectively.*

THE POSSIBILITIES AND ADVANTAGES inherent in a unified program of high school metallurgical education have not been generally apparent. Probably because of our admitted shortage of trained metallurgists, emphasis has been placed largely on developing our currently inadequate facilities for providing college training in metallurgy.

Yet the pressure on the universities to increase the number and extent of their metallurgical courses has come entirely from industry, and not at all from prospective students. And, taking the broadest view, it is therefore entirely possible that our present shortage of trained metallurgists exists because only an insignificant number of boys, before they go to college, have any conception of the nature and opportunities of a professional career in the metallurgical arts and sciences. Teaching metallurgy in the high school should be a powerful factor in increasing the number of metallurgical students in colleges.

In addition to acquainting youngsters with the possibilities in metallurgy before they select their careers, high school metallurgical training has other advantages. Even if only academic, such courses offer an excellent preliminary groundwork for those who may go on to study the subject in college. And, if supplemented by actual laboratory practice, this training provides qualified assistants for industrial metallurgical laboratories, most of whom continue their study at night. Those boys that enter industrial production work directly from high school often find their knowledge of metallurgy of distinct personal advantage in earning promotions to supervisory positions. Some employers' reactions are cited at the end of this article.

Pouring a Casting in the Foundry at Brooklyn Technical High School.



General Nature of the Courses

The number of high schools giving metallurgical or related courses is not large, but some seem to have attained such striking success that a detailed description of their equipment and curricula appears warranted. The equipment available, for example, at the Brooklyn Technical High School, the Buffalo Technical High School and Cass Technical High School (Detroit) is so extensive as to be the possible envy of many colleges. In this article the work at Brooklyn Tech is featured—for several reasons. This school appears to have been somewhat of a pioneer in offering metallurgical courses, and its methods and equipment are therefore among the most highly developed. At the same time they may well serve as a pattern for high schools considering the introduction of metallurgical teaching.

In none of the high schools is metallurgy taught as a separate curriculum, complete in itself, nor is it always called "metallurgy." At Brooklyn, the metallurgical work is distributed among the heat treatment laboratory, the foundry and the materials testing department, all part of the mechanical curriculum; at Buffalo, much of the metallurgy is taught in the metal processing and metallography courses, which are part of the industrial chemistry curriculum, and in foundry practice and materials testing, units of the mechanical curriculum; at Cass, metallurgy comes closest to autonomy, for here it is, as "Metallurgy", not only required of students in the mechanic arts, automotive, aeronautics and science courses, but is a feature of the joint chemical-metallurgical curriculum. Foundry practice at Cass is taught in the general metal work and pattern-making curriculum. In all cases the practical phases (foundry work, for example) are given in the first, second or third years, and the more technical (metallography and heat treatment) in the fourth.

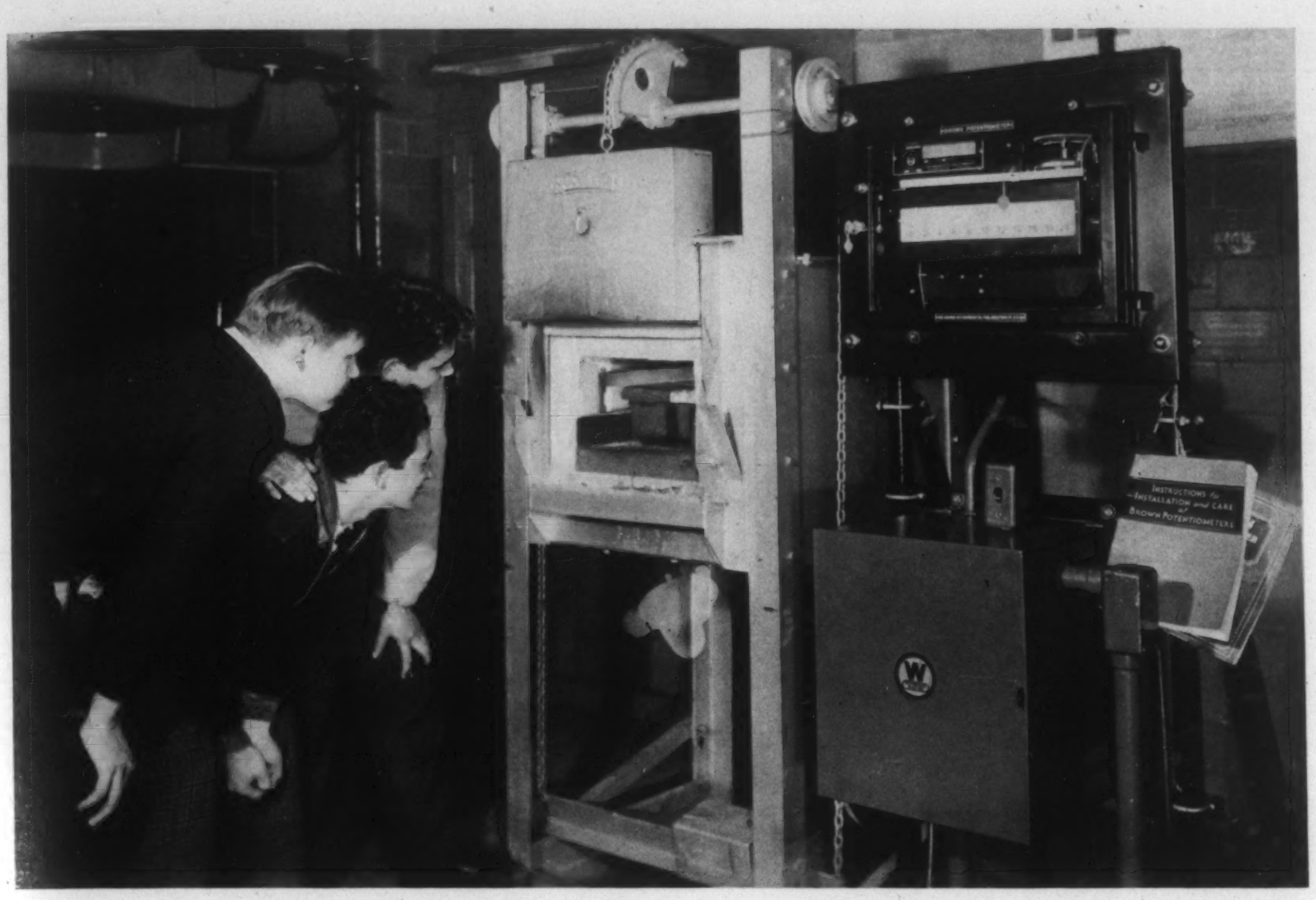
Metallurgy at "Brooklyn Tech"

Brooklyn Technical High School is a school of applied science, the only polytechnic high school in New York City chartered and approved by the State Department of Education. The school prepares boys for colleges of engineering, architecture and applied science, or for direct entrance into technical work through "unit technical" or "terminal" courses (which include the metallurgical subjects) that are offered to qualified students during their last two years. No narrow specialization is permitted; on the contrary, the aim is to give a broad foundational training in science and technology, with a good general secondary school education.

The student selecting the four-year mechanical course follows, for his last two years, a program that includes foundry practice, physical testing, heat treatment of metals, photomicrography and X-ray work. These provide a completely coordinated series of related courses in the field of metallurgy, which, it is believed, can successfully replace some of the work ordinarily taken in the early years of college.

The foundry equipment at Brooklyn is surprisingly complete, for it includes a 2-ton cupola, a 250-lb. Ajax-Northrup coreless induction furnace, a Pittsburgh Lectromelt 3-phase furnace and some gas-heated furnaces for low-melting non-ferrous alloys, Associated with the foundry are the cleaning rooms, sand blasting equipment, and pattern storage facilities. Sand, purchased in carload lots, is conditioned and tested with the most advanced apparatus available today. Students taking the course are required to understand the construction and operation of these furnaces and equipment, which they do through instruction and observation and by direct practice in sand handling, molding, core-making and drying, cleaning of castings, etc. Castings, which range in weight from a few

Instruction in Cupola Operation at Brooklyn.



Heat-Treating Furnace and Control at Brooklyn.

ounces to something over 450 lbs., are used by the school's machine shop, and other departments of the school.

Physical testing is conducted in a strength of materials laboratory completely fitted for this type of work. Tension, compression, torsion, impact and fatigue tests are routine procedure; most of the testing machines are autographic.

The Heat Treatment Laboratory

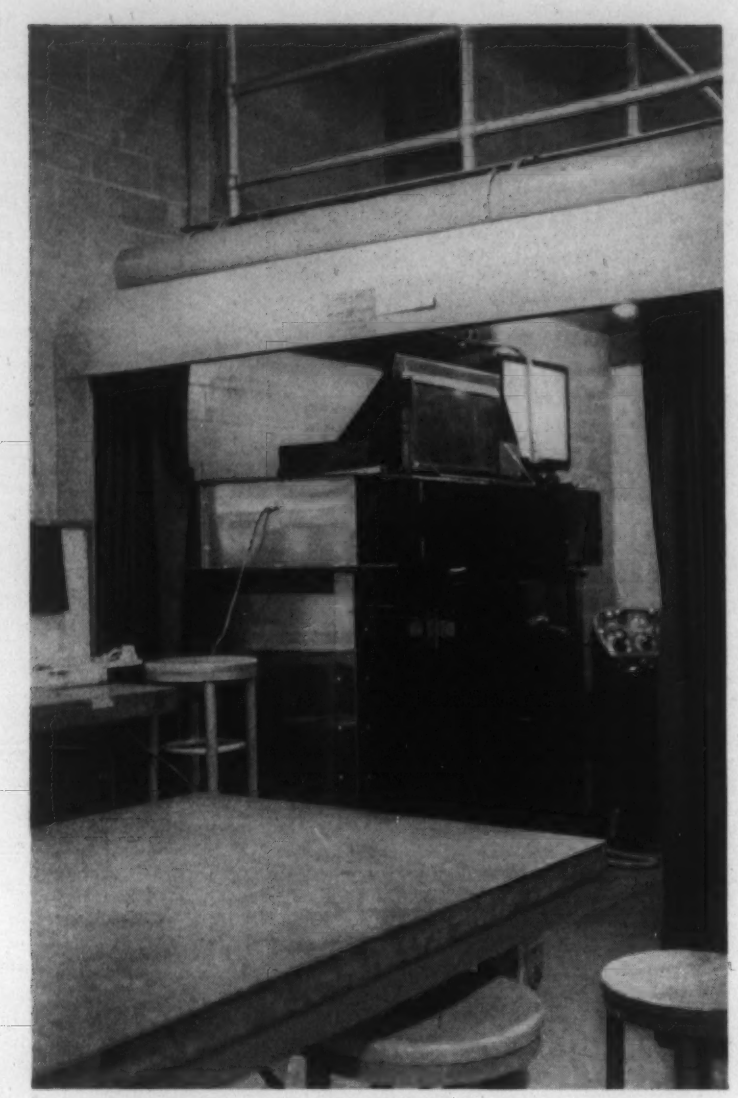
The equipment in the heat treatment laboratory, however, is the outstanding feature. Students polish specimens on modern direct-driven polishing machines, do their own etching, observe each sample under 1 of 12 metallurgical microscopes or photograph it with 1 of 2 photomicrographic cameras, which are equipped for macrophotography on one hand or for high power work with ultra-violet light and quartz lenses on the other. Specimens are bakelite-mounted when desirable. There is a completely equipped dark room where developing, printing with an automatic machine, and enlarging to 40 x 48 in. is done. Three colors of light are available and special provision is made for developing X-ray films. Facilities are at hand for the production of lantern slides in quantity.

In the laboratory are two X-ray machines—a portable 100 Kv. machine, and a larger 200 Kv unit. This equipment is used by the students not only to inspect welds and castings, but also for the production and observation of diffraction patterns and the elucidation of crystal structures.

The laboratory is also equipped with a box type electric muffle furnace with potentiometer pyrometer, a laboratory size high-frequency induction furnace for the preparation of small melts, a high temperature furnace, and equipment for polar-coördinate recording of the critical points of steel. Important, though less spectacular, are several laboratory annealing furnaces, Rockwell, Brinell and Scleroscope hardness testers, grinders, a hot plate for tempering, oxy-acetylene apparatus, an optical pyrometer and other necessary adjuncts to a metallurgical laboratory.

The academic background of the heat treatment course covers the selection, manufacture and treatment, and metallographic inspection of the various irons, steels and nonferrous metals and alloys of industrial importance. In studying the equipment, an understanding of its operation rather than manipulative skill is the aim. In each laboratory session, a single unit, for example the metallographic camera, is studied, and the student, after assisting in its use, and observing the microstructure of a suitably prepared sample, prepares a sketch and description of the apparatus, together with a free-hand reproduction of the microstructure as he saw it. Another session may be devoted to the properties and heat treatment of a hypereutectoid steel, and from observation and instruction the students grasp the significance of the critical points, the nature of the microconstituents in such a steel and their effect, under a few heat treatments, on the ultimate properties.

This laboraory cooperates with other departments of New York City in many ways, and has examined for them a variety of materials, ranging from chisels to bridge reinforcements. No commercial work is undertaken, but problems of educational value are welcomed for study and solution.



200 Kv. X-Ray Machine Used at Brooklyn.

Transformers and Circulating System for 35 Kw. High-frequency Induction Furnace at Brooklyn.

At Other High Schools

Excellent metallurgical courses are given also at Buffalo Technical High School and Cass Technical High School, Detroit. Several others, notably Central Technical School, Toronto, Lane Technical High School, Chicago, and West Technical High School, Cleveland, offer a certain amount of instruction in metallurgy, though in less comprehensive fashion.

The metallurgical subjects at Buffalo, although scattered in several curricula so that no one student takes them all, are unusually extensive, covering the fundamentals of production, testing, properties, heat treatment, structure and metallographic examination of ferrous metals; a full year of metallography is offered to post graduate students. Foundry practice and materials testing are included in another curriculum.

The heat treatment equipment at Buffalo, although not so extensive as that at Brooklyn, is still unusual for a high school, and includes two photomicrographic cameras, three metallurgical microscopes, hardness testers, recording and optical pyrometers, muffle, pot and tempering furnaces, together with all necessary grinding and polishing equipment.

Cass Technical High School, Detroit, located in the heart of one of the most important metal working and treating communities in the world, has developed its metallurgical instruction accordingly. Students who select the chemical-metallurgical curriculum take a full year of metallurgy, with ten 45-min. periods per week. A half-year course is given to students in certain other curricula. In addition, advanced work in metallurgy is offered in the evening school.

The metallurgical instruction at Cass is as thorough and comprehensive as can be found in any high school. The time allotment is much greater than that at the other schools, so that greater attention to detail is permissible. The list of topics covered reads like the chapter headings in a good elementary college textbook on the subject, and includes production, treatment, properties and microstructure, testing and uses of irons, steels, alloy steels, copper, bronzes, brasses, aluminum alloys and other alloys.

The laboratory at Cass is also well equipped, with one photomicrographic camera, six metallurgical microscopes, polishing machines, photographic developing and printing apparatus, four electric furnaces with indicating pyrometers, one recording pyrometer, a tensile tester, three types of hardness testers, etc.

Viewpoints on High School Metallurgy

Enough has been written to show clearly the scope, extent and experimental facilities of the metallurgical courses given at some pioneering technical high schools. For those of us that "discovered" metallurgy somewhere from three to ten years after we were out of high school, the surprise at knowing the subject is now taught in certain secondary schools is probably exceeded only by shock at realizing that the equipment at some of the high schools is much more extensive than any we ever personally handled in college or industry. The real question, however, centers about the actual value of such preliminary metallurgical instruction to the industry and science it is designed to serve.

To determine this, the editors of METALS AND ALLOYS independently questioned several employers of graduates

Mr. McArdle and One of His Students Using the Photomicrographic Equipment.

in the mechanical course of Brooklyn Technical High School. The answers showed an interesting division of opinion, according to whether the company employed the graduates in actual metallurgical work or in some unrelated phase of mechanical engineering. Where the boys were not used metallurgically, the employer invariably felt that the general technical background possessed by the school's graduates was much more useful than any specific knowledge of metallurgy they might have gained. Typical of these was this answer from George Rattray, of Fairchild Aerial Camera Corp., who said: "The general value of such education for students intending to follow the engineering profession is very great, and we believe the system to be more than worth while in its contribution to the manufacturing industry generally."

Those companies, however, that used the graduates in actual metallurgical work were enthusiastic about the value of their training. J. L. McClane, of Seversky Aircraft Corp., states that the boys have a very good understanding of metallurgical equipment, that one of them eventually assumed charge of all physical testing equipment, and that if the boys in his employ are typical, the training is of real value. This sentiment is echoed by G. B. Back, Jr., of New York Testing Laboratories, who writes that his experience shows "the high schools are doing a wonderful job in their teaching of metallurgy and allied subjects."

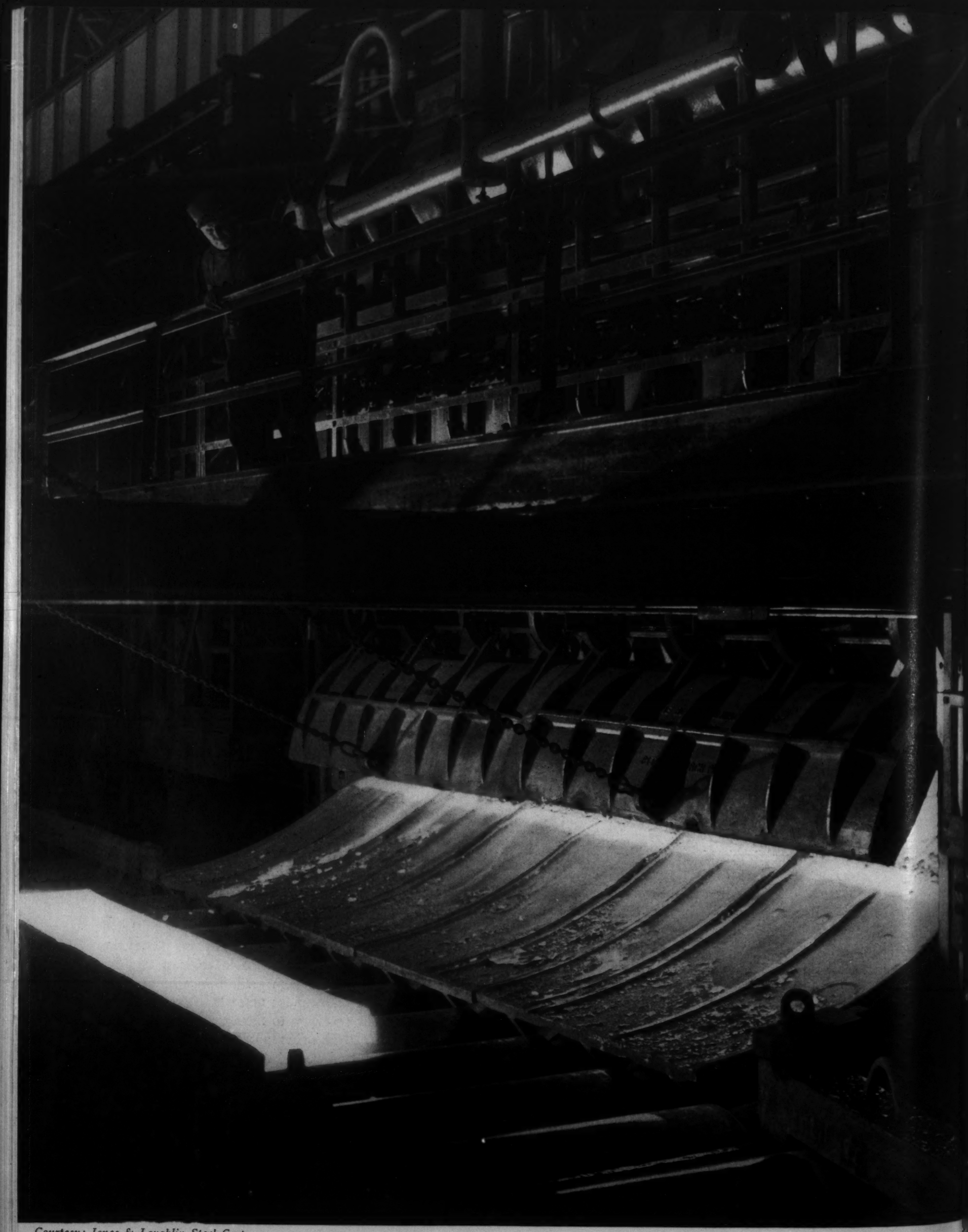
This article may well be closed with the answer received from the head of a very large metallurgical research laboratory in the New York metropolitan territory:

"Within the past two or three years we have given employment to six graduates or students of the Brooklyn Technical High School, all for jobs which might be described as technical assistant or helper to college trained metallurgists or chemists.

"At the beginning these boys are expected to take care of many of the routine details of metallurgical laboratory work and to assist, under close direction, in some of the more elaborate experimental undertakings. As time goes on they are given opportunities to specialize and qualify as technicians able to carry on with only moderate guidance.

"Our experience has really been gratifying. The fear that such advanced technological training is over the heads of these boys or is wasted upon them is entirely mistaken. On the contrary, the excellent equipment and instruction of this secondary school seems to do at least two important things. It attracts high grade boys who are technically inclined and who cannot normally expect to attend a university, and by revealing to them early how the metal industries can use them, sifts out those who are really adapted for this sort of work. At any rate, the result is a group of youngsters who have a maturity of outlook which is interesting and who know why they want a metallurgical job. Their later development has been good and the majority of them are taking university extension courses leading toward a degree.

"We and other local industries need boys qualified for these junior responsibilities, and we are fortunate to have a school which is so successfully supplying this need."



Courtesy: Jones & Laughlin Steel Corp.

First Step in Rolling Hot Strip: Steel Slab Leaves Heating Furnace on Its Way to First Rolling Operation.

COMPARATIVE EFFECTS OF

Controlled Atmospheres

ON ALLOY AND CARBON STEELS

Part II

(Concluded from February Issue)

by E. E. Slowter and B. W. Gonser

Chemical Engineer and Metallurgist, Respectively, Battelle Memorial Institute, Columbus, Ohio.

DISCUSSION OF RESULTS

Atmospheres

THE pure nitrogen atmosphere was selected not because of its commercial possibilities but because it offered a base line for comparison. In this atmosphere the action on all the steels was practically nil, being just faintly on the decarburizing side. Even with extreme care in purification, it was almost impossible to eliminate traces of temper colors.

The dilute CO-N_2 atmosphere which had previously been found to be very satisfactory for plain carbon steels was almost equally satisfactory with the alloy steels. The very slight action was faintly decarburizing as in the case of pure N_2 but the prevention of temper colors was much simpler because of the presence of CO. Although entirely satisfactory from the standpoint of decarburization, dilute CO formed an oxidized film over chromium steels, hence is unsuitable for use in those few cases where a bright surface is essential on such steels. Gains in weight by the

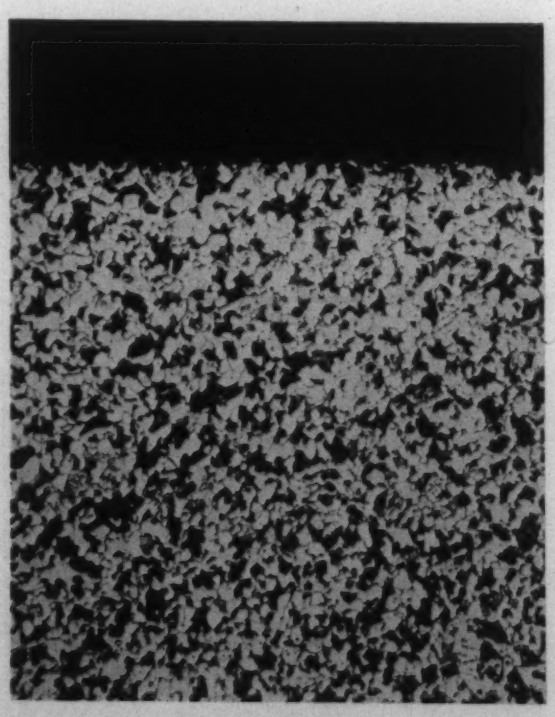


Fig. 13. Plain 0.44 C Steel (Sample H) Wt. Change: — 0.00004 g. per sq. cm.; blue-black surface.

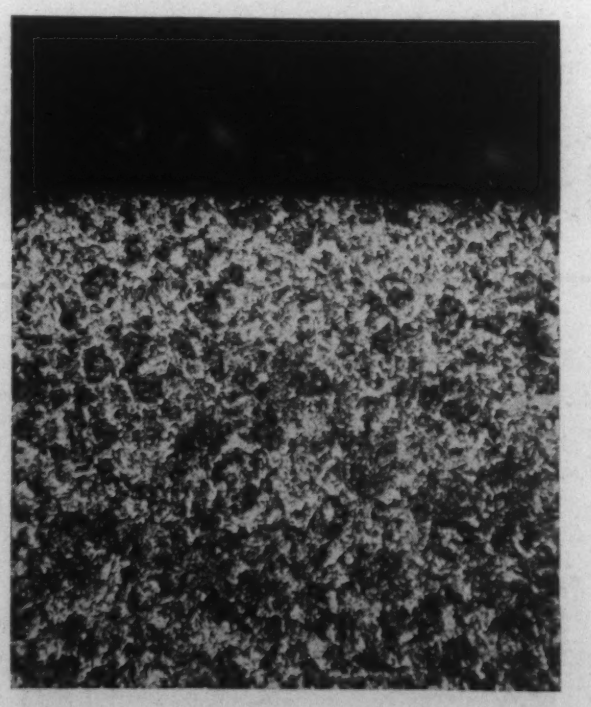


Fig. 14. SAE 3250 NiCr Steel (Sample N) Wt. Change: — 0.00013 g. per sq. cm.

Negligible Decarburizing Tendency of a Dried, Partly Burned Natural Gas Atmosphere after 3 hrs. at 800 deg. C. (1472 deg. F.). Weight changes due to slight oxidized films do not appear to be important. In these, as in practically all similar tests, a change in weight of the sample normally indicates carburization or decarburization to the approximate extent of the weight change. 100 X. Etched with 1 per cent Nital.

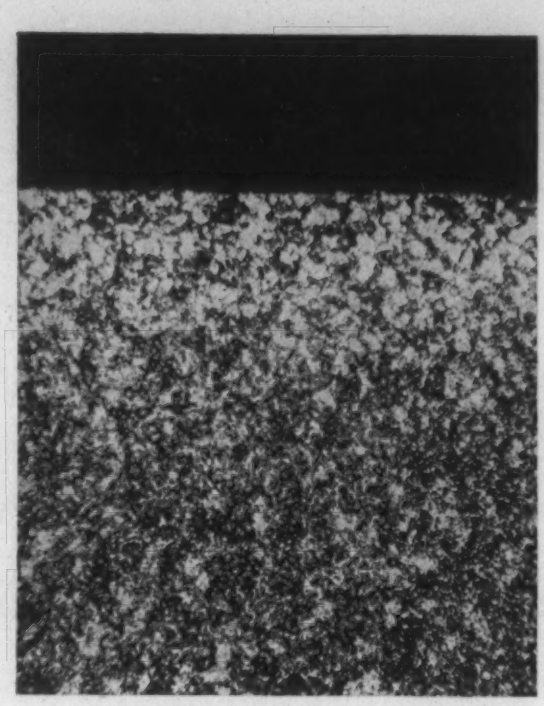


Fig. 15. Decarburization in Dried, Partly Burned Natural Gas with CO_2 Not Removed. Wt. Change: — 0.00054 g. per sq. cm.; blue surface.

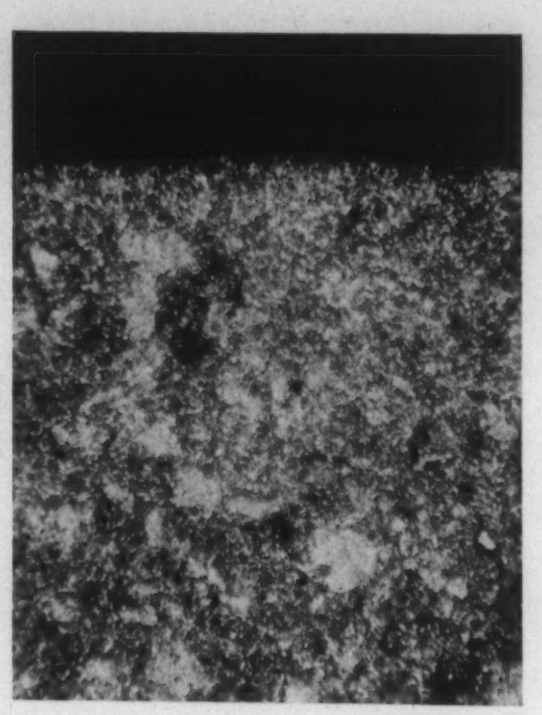


Fig. 16. Negligible Carburization in Dry, CO_2 Free, Partly Burned Natural Gas. Wt. Change: + 0.00029 g. per sq. cm.; heavy green film.

Prevention of the Decarburization of a High Carbon Alloy Steel (S.A.E. 521000, Sample M) by the Removal of CO_2 and H_2O from a Partly Burned Gas. Treatment 3 hrs. at 800 deg C. (1472 deg. F.) 100 X. Etched with 1 per cent Nital.

very high chromium steels (16-18% Cr) in dilute CO were found by microexamination to be due largely to carburization but to a slight extent to the oxidized surface film. Low Cr steels (around 1 per cent), although staining slightly, appear to act toward carburization and decarburization in a manner similar to other steels of the same carbon content. The elimination of the faint decarburizing action of 5 per cent CO-N_2 alone is apparently easily accomplished for all steels by the addition of small amounts of methane.

Dilute H_2-N_2 is just slightly more decarburizing to all of the steels than pure N_2 though the prevention of temper colors is of course much easier. Its action was about the same on all the alloys, being somewhat greater as the carbon content of the alloy increased. The addition of a small amount of CH_4 to this atmosphere is sufficient to put it on the carburizing side.

A dilute CO-H_2-N_2 atmosphere with about 1 per cent CH_4 added was carburizing to all of the steels. The action was greater than in any of the previously discussed atmospheres because of the smaller N_2 content but for any given carbon content of any of the alloys an atmosphere producing no decarburization could be obtained by proper adjustment of the CH_4 content. Obviously, propane or butane could be used as well as methane, although carbon deposition or the tendency for such higher hydrocarbons to decompose would be greater than with methane. The amount of carburization produced in any given steel by this atmosphere appeared to be dependent upon the carbon content of the steel, just as in the case of the plain carbon steels.

The undried generator gas was decarburizing to all steels, except those of quite low carbon contents, even at the lowest temperature used—1472 deg. F. (800 deg. C.). At that temperature the alloy steels appeared somewhat more resistant to decarburization than the plain carbon steels but at higher temperatures this difference was not apparent.

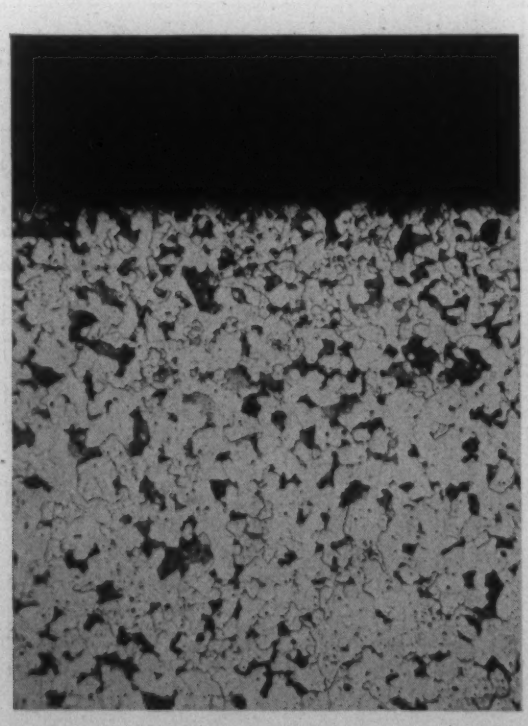


Fig. 17. Cu-Ni Low Alloy Steel (Sample W) Wt. Change: + 0.00074 g. per sq. cm.; slightly reduced reflectivity of surface.

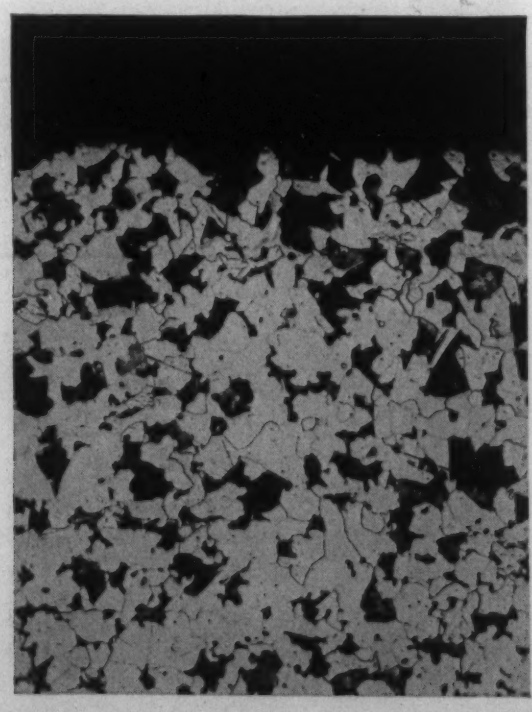


Fig. 18. Cr-Cu Low Alloy Steel (Sample X) Wt. Change: + 0.00088 g per sq. cm. Green surface film.

Carburization of Low Alloy Steels in Dry, CO_2 Free Partly Burned Natural Gas after 3 hrs. at 950 deg. C. (1742 deg. F.). This carburizing tendency can be eliminated by adjustment of the gas composition. The chromium steel is slightly carburized in spite of an oxide film over its surface. 100 X. Etched with 1 per cent Nital.

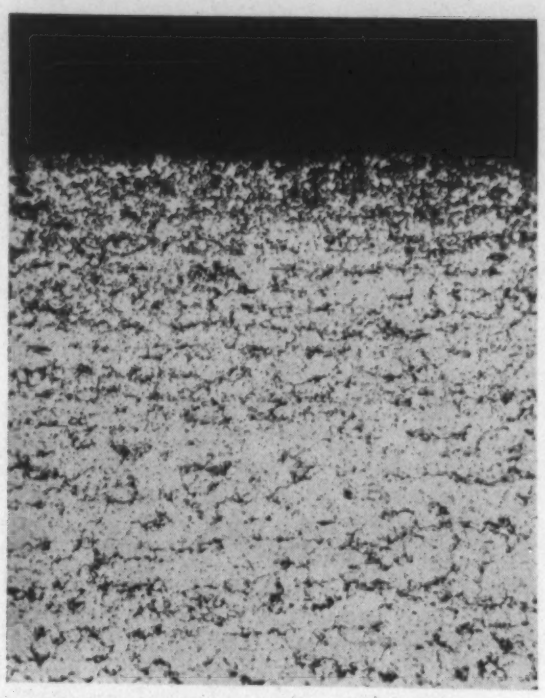


Fig. 19. Atmosphere of 5 per cent CO, Balance N_2. Wt. Change: + 0.00064 g per sq. cm.; heavy green surface film.

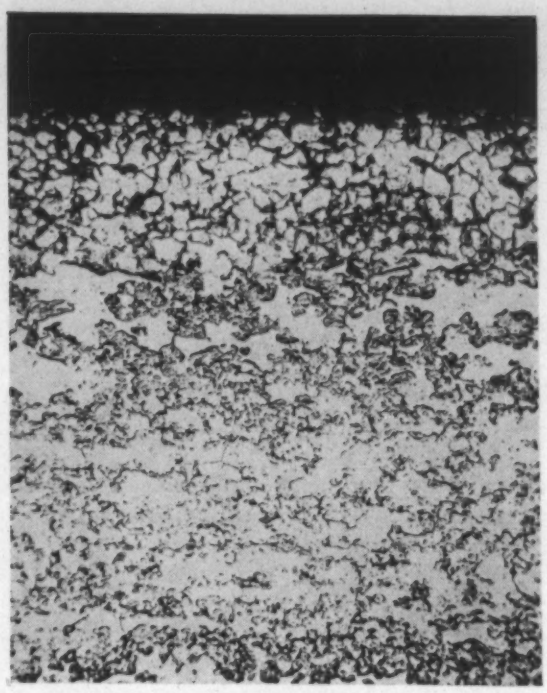


Fig. 20. Atmosphere of Dry, CO_2 Free, Partly Burned Natural Gas. Wt. Change: + 0.00131 g per sq. cm.; thin green film.

Carburization of a 17 per cent Chromium Steel (S.A.E. 51710—Sample Z) Beneath the Oxide Surface Film. Treatment: 3 hrs. at 900 deg. C. (1652 deg. F.). 100 X. Etched with 10 per cent acidified ferric chloride.

In all cases the samples were covered with a black film.

The dried generator gas was very similar in its action to the undried gas except at the lowest temperature, 1472 deg. F. (800 deg. C.), where its decarburizing action was materially lessened. This would be expected from the nature of the gas reaction previously discussed.

$$CO_2 + H_2 = CO + H_2O$$

As has been pointed out, in a dry gas this reaction is driven towards the right but at temperatures of 1472 deg. F. (800 deg. C.) and lower, the rate is quite slow so that the acceleration of decarburization due to the presence of water vapor at such temperatures may be minimized by drying the partly burned gas. If, however, it is to be used at higher temperatures, considerable water vapor is produced by this reaction and the gas behaves in practically the same manner as an originally wet gas.

With the dried, CO_2-free generator gas the above reaction is stopped because of the absence of CO_2 and the gas behaves as a mixture of CO, H_2, CH_4 and N_2 might be expected to, i. e. this gas is non-reactive within itself and is rather easily made neutral to any carbon or alloy steel by adjustment of the CH_4 content. The similarity between the synthetically mixed CO, H_2, CH_4, N_2 mixture and that prepared from the generator gas can be seen from a comparison of Figs. 6 and 9. That prepared from the generator appears somewhat more intense in its carburizing and decarburizing tendencies. In both cases the alloy steels appear somewhat more resistant to carburization at 1472 deg. F. (800 deg. C.) than the plain carbon steels but this difference was not noticeable at the higher temperatures. This dried, CO_2-free generator atmosphere gave much superior surfaces to those obtained in the dried and undried gas. The black films were entirely absent and only occasional temper colors were noted.

Steels

First of all, it should be noted that, with a few exceptions, the behavior of the various alloy steels was practically dependent upon the carbon content of the steel in much the same manner as plain carbon steels. At the lowest temperature of 1472 deg. F. (800 deg. C.) the various alloy steels exhibited slightly better resistance to change, either carburization or decarburization, than the plain carbon steels. This was not noticeable at either of the higher temperatures.

The high chromium alloys all behaved quite differently from the remainder of the steels. In no case did any of these specimens lose weight and in all the atmospheres except that of 10 per cent H_2, 2 per cent CH_4, balance N_2, green staining was observed. The chromium seems to have a great affinity for oxygen, even being oxidized in the presence of CO which for most steels is a reducing rather than an oxidizing agent. The low chromium steels have a great tendency toward the formation of a faint blue film on their surfaces during heat treating while the nickel steels appeared more resistant than the ordinary carbon steels toward any film formation. However, these differences in surface appearance did not connote any differences in propensities toward carburization and decarburization.

The only other steels to show any abnormalities were the silicon steels. The high silicon ($3\frac{1}{2}$ to $4\frac{1}{4}$ per cent Si) transformer sheet was very low in carbon (0.03 per cent) and hence, without the silicon, should have been carburized readily. However, under no conditions was any appreciable carburization noted; in fact it appeared to be entirely prevented by the silicon. The silico-manganese spring steel (SAE 9250) behaved in a somewhat similar manner since it appeared to be more resistant to both carburization and decarburization than an ordinary plain carbon steel of equal carbon content. It showed the expected decarburization in dried and undried generator gas, but when both H_2O and CO_2 were eliminated, the decarburization to which this steel is prone when heated in air, was eliminated. It would appear that controlled-atmosphere hardening of silico-manganese springs offers real promise.

From what has been said it appears that the complete removal of CO_2 as well as of H_2O from the ordinary partly burned or generator gas commonly used for bright annealing is a prerequisite to satisfactory application of such gas to hardening without decarburization.

Resistors and Furnace Parts

This work has a bearing on the behavior of resistors, furnace parts, and the like, made of high Cr, heat resistant

alloys, where an oxide film of suitable properties may be protective while one of other properties may be deleterious. The data so far reported deal with the effect of the atmosphere upon the steel being treated. The effect of the atmosphere upon the furnace, also, cannot be neglected and forms another phase of the general investigation upon which work is now in progress.

CONCLUSIONS

IN regard to the atmospheres which may be used on a wide variety of alloy steels it may be said that:

1. CO_2 and H_2O are just as detrimental to medium and high carbon alloy steels as to plain medium and high carbon steels and their complete removal from a heat-treating atmosphere is desirable for the same reasons.
2. Dried partly combusted gases are just as severe in their action on carbon and alloy steels at temperatures over about 1,600 deg. F. as the undried gases but are somewhat milder in their action at lower temperatures.
3. With a few exceptions, any atmosphere which is suitable for a range of carbon steels is also suitable for a similar range of alloy steels of the same carbon contents.

As for the various alloy steels, it appears that:

1. The majority of alloy steels behave in approximately the same manner as plain carbon steels of the same carbon content, the alloy steels often being slightly more resistant to change, especially at the lower temperatures.
2. Steels containing relatively large amounts of silicon are more resistant to change, either carburization or decarburization, than plain carbon steels of equal carbon content.
3. Both high and low chromium steels are especially susceptible to oxygen-containing gases, extreme care in the removal of the latter being necessary if prevention of all oxidation is desired. Even CO may give up its oxygen to chromium-bearing alloys.
4. Nickel steels are slightly more resistant to filming or fogging during heat treatment than ordinary carbon steels while low chromium steels are much less resistant. These films do not materially affect the rate of carburization, or decarburization, so from the point of view of hardening rather than of appearance, they should not influence the choice of the atmosphere.

Editorial Comment *(Continued from page A 27)*

bearing metals will not serve, Ag may lift the bearing metal ceiling once more.

Considerable automotive use is made of corrosion-resistant Pb-base babbitt, of an old type, not the Pb alloy with alkali and alkaline earth metals that finds some railway use. Even the In-treatment applied to the latter has not made it corrosion resistant. It is interesting to note, however, that the prediction of a few years ago, that the day of Sn-base babbitt in auto engines was past, has not been fulfilled. Neither the old Cu-Pb nor the newer Cd-base alloys have appreciably displaced it.

However, with the knowledge that Cd and Ag are bearing metals and that the latter works well pure,—not requiring the classical "hard particles in a soft matrix,"—and with the advent of cast and of surface-hardened crankshafts that bring variety into the shaft, as well as the bearing,—the bearing game is cracked wide open. Smart's ingenious stunt shows that an apparent difficulty can be surmounted in this, as in other metallurgical fields. It may also encourage more attention to plating as a means of making a desired bearing surface, a matter long ago suggested and one that other experiments some years ago showed to contain possibilities not yet generally recognized.

Perhaps some Steinmetz will come along to tell us just what an ideal bearing should have, not only in the bearing face but in the bearing back and the shaft also. If we really knew these things, we might handle the metallurgy accordingly.—H.W.G.

Secrets

Col. Rose of the Gray Iron Founders' Society tells a story about 60 big shots in the petroleum industry who agreed to submit their most valuable secret to a confidential agency. The summary showed 57 of the 60 "secrets" to be identical. The remarkable thing about this is not that everybody had the "secret", but that they rated it at the top of the list.

Instead of trying to keep secrets that can't be wholly kept, the modern way is to swap complete information. A willingness to swap information and to attack jointly the problems that are truly common has long been evident in the committees of technical societies. Indeed such committees can only command the time that service on them requires because each individual in them feels that, in the long run, he gets more than he gives. Incidentally, the most effective committees are those in which membership is for a limited term so, if a sponger happens to obtain membership, he can be expunged in due course.

Trade associations and smaller less formal groups within an industry, who have mutual interests and mutual problems are increasingly swapping so called technical secrets. Moreover when they find that they need information that nobody has in sufficiently complete form, they are more and more setting out to get it by joint action. No law has yet been passed to hamper this sort of thing. From a purely selfish point of view the leaders in an industry generally find it wise to help a weak sister whose product is of poor quality or whose salesmen, through ignorance of facts, are passing out erroneous information, such as claims for properties that cannot be substantiated. The poor products or the misinformation injure not only the erring firm, but all competing firms, since the user in whose hands the products fail, or who misapplies them because of extravagant claims for their utility, is quite likely to turn to a substitute.—H.W.G.

THE MECHANICAL PROPERTIES OF

Copper at Elevated Temperatures

by C. H. Lorig, F. B. Dahle, and D. A. Roberts

Mr. Lorig is Supervising Metallurgist and Messrs. Dahle and Roberts are Metallurgists, Battelle Memorial Institute, Columbus, Ohio.

IN AN INVESTIGATION ON COPPER for ingot molds and stools for the United States Metals Refining Co., an opportunity was afforded to determine the mechanical properties of copper at elevated temperatures. The present investigation was made to obtain information which may be useful for determining what type of copper would serve best for the purpose in mind. The authors are indebted to the United States Metals Refining Co., for permission to publish the results.

Material

Three types of copper, namely, oxygen-free, high-conductivity; phosphorized oxygen-free, high conductivity; and tough-pitch, were received from the refinery for the high-temperature tests. The copper was received as sections 8 in. high by 4 in. thick and 13 in. long, cut from the center portion of 400-lb. cast cakes measuring 13 in. by 26 in. by 4 in. The center section of large cakes was thought to give more uniform specimens, and consequently provide more reliable test data.

The locations from which the specimens were taken are shown in Fig. 1. The center lines of the tensile specimens were located in planes 1 in. from either side of the cakes so that the crystals of the specimens would be normal to the long axis and closely alike in specimens from a given cake. The center of the cakes (where the crystals converge) and the two end slabs were discarded. The impact specimens were cut so that the Charpy key-hole notch was normal to the columnar crystals extending in from the side of the cakes.

Etched sections of the three copper cakes are shown in Fig. 2, 3 and 4. Both the oxygen-free and the phosphorized copper show long columnar grains extending in from the surface. There is some discontinuity in the grain structure of the tough-pitch copper, however.

A great deal of care was taken in the machining of the test specimens, inasmuch as cold working of copper may cause some recrystallization upon heating. The specimens were not ground or polished. A lathe tool taking a very light cut was used in finishing the gage length and shoulders of the tensile specimens to avoid distorting the surface.

Representative specimens from the cake are shown in Fig. 5. These specimens were etched in nitric acid to bring out the grain structure. It will be observed from the etched structure that the grain size in the tough pitch copper specimen was slightly smaller than that in the other two.

Tensile Tests

Properties of Cast Copper: The tensile tests at elevated temperatures were made in accordance with the tentative standards set up by the A.S.T.M.-A.S.M.E. Joint High-Temperature Committee (ASTM: 21-34T). These standards require a minimum temperature gradient of 5 deg. F.

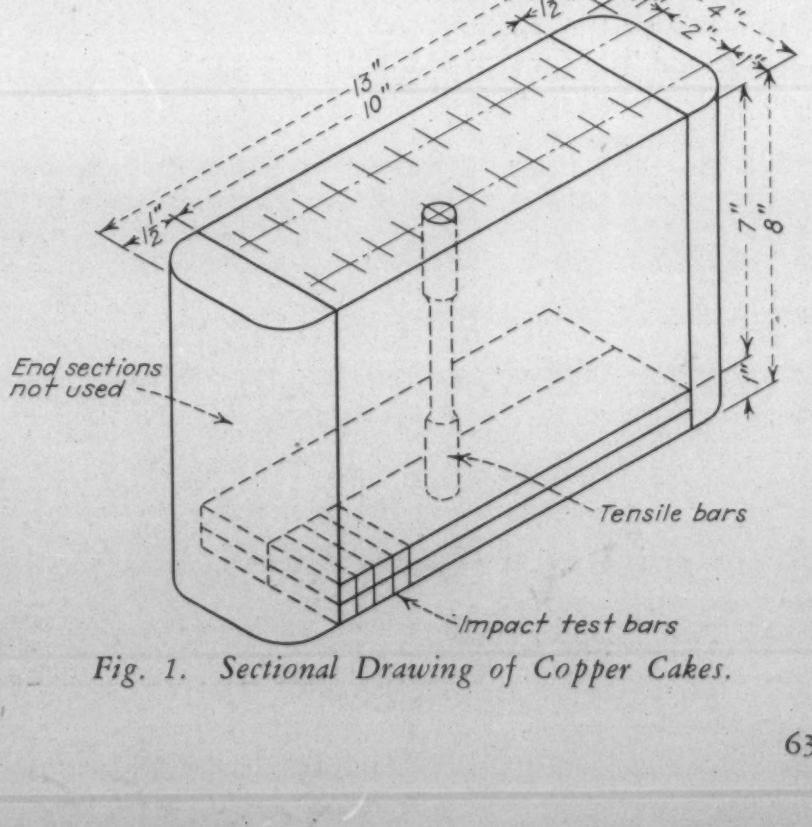


Fig. 1. Sectional Drawing of Copper Cakes.

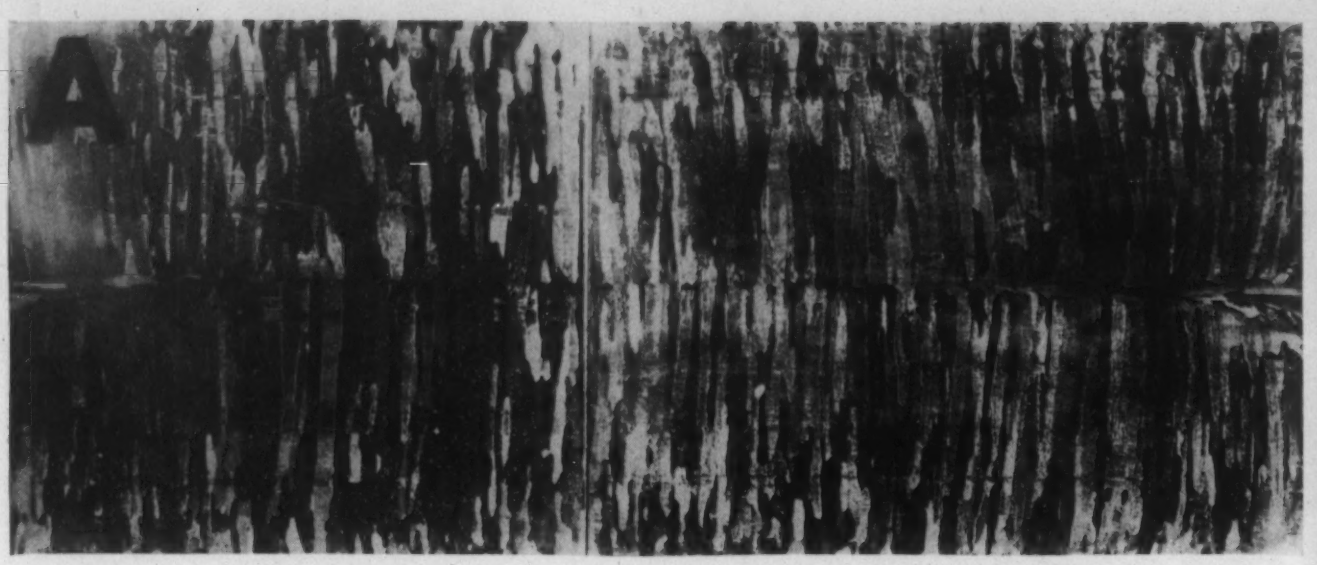


Fig. 2. Etched Section from the Top of Oxygen-Free High Conductivity Copper Cake.

over the gage length of the specimen. In calibrating the furnace for temperature uniformity, a dummy tensile specimen of copper, in which thermocouples were inserted in holes located at the center of the gage length and also at points 1 in. to either side of the center, was used. Two other thermocouples were located in the shoulders of the specimen just beyond the reduced section and were inserted through axial holes drilled in the ends of the specimen.

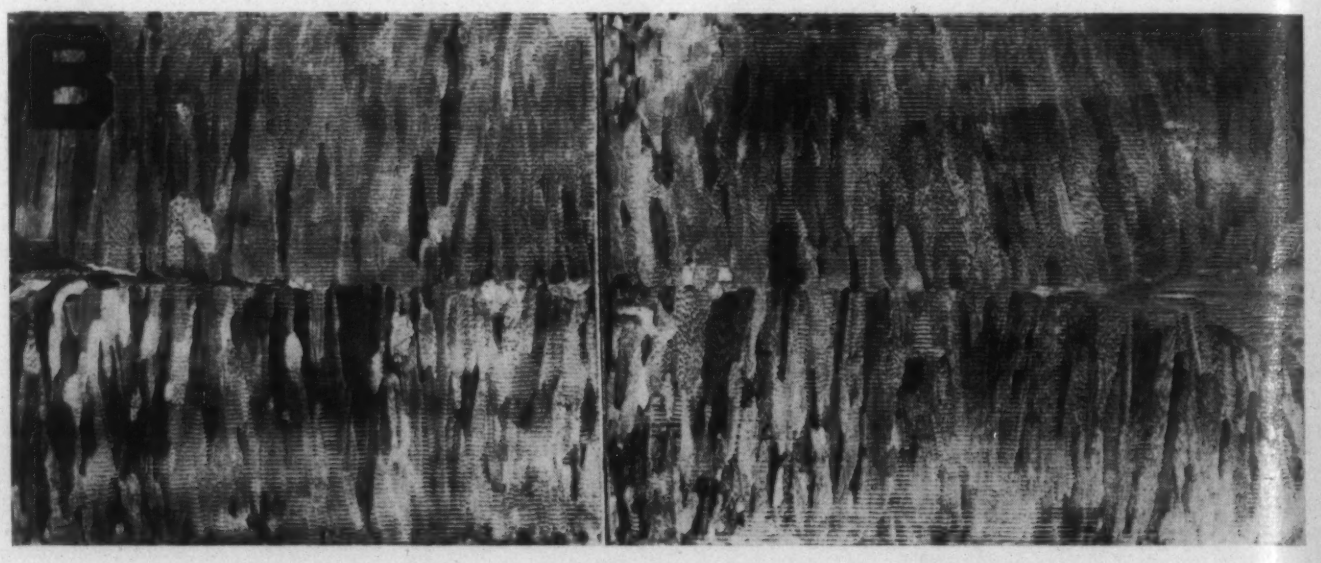


Fig. 3. Etched Section from the Top of Phosphorized Oxygen-Free Copper Cake.

As these two thermocouples were used for controlling the temperature during actual testing, it was necessary to know the relation between these couple temperatures and the temperatures measured by the three gage-length couples. Calibrations at all the test temperatures showed a temperature uniformity well within the limits set up by the Committee.

In making a test, specimens were heated to the test temperature and held for a period of ½ hr. before testing. Although it is usual in tests of this nature to hold the specimens for 1 hr. before breaking, it was felt that, since copper has such a high thermal conductivity, ½ hr. would be ample time to insure temperature equilibrium. The results obtained in testing the as-cast bars are shown in Table I and Fig. 6.

Tensile strengths in the three types of cast copper show a gradual falling off with increase of temperature. There is no great difference in the strengths of the copper, although the phosphorized is a little better at the higher temperatures. This tendency for the strength to decrease slowly and uniformly with temperature was unexpected in view of the trend of tensile strength-temperature curves recorded for unannealed wrought copper and for other metals.

In order to show better the type of fractures obtained in the cast bars at the various test temperatures, representative broken specimens have been photographed. These are

Fig. 4. Etched Section from the Top of Tough Pitch Copper Cake.

shown in Figs. 7, 8, 9, 10, and 11. In Fig. 7 are shown broken test bars after testing at 300 deg. F. The types of fracture obtained at the lower temperatures were woody in appearance. At the higher temperatures, as may be seen from other figures the oxygen-free copper and the tough-pitch copper had crystalline fractures. The phosphorized copper, on the other hand, nicked down and showed considerably more ductility at the high temperatures.

Specimens broken at 550 deg. F. are shown in Fig. 8. Of particular interest in these and in specimens shown in Figs. 9, 10, and 11 are the cracks which formed along the gage length on either side of the fracture. These cracks seem to be at grain boundaries and apparently are indicative of low ductility at the higher temperatures. It will be observed that the phosphorized copper shows the least

Table I. Tensile Test Data on Cast Copper*

Test Temp., Deg. F.	Ultimate Strength, Lbs. per sq. in.	Elongation, per cent	Red. of Area,** per cent	Charpy Impact, Ft.-Lb.
Oxygen-Free High-Conductivity Copper:				
R.T.	21,800	54.7	80.8	35.8
200	16,850	47.3	76.9	32.3
300	16,450	50.3	69.8	30.1
400	15,275	31.3	38.3	27.3
500				31.5
550	11,325	16.5	18.6	
600				31.5
700	10,325	19.0	17.8	29.8
850	8,825	14.8	20.9	29.2
1000	6,400	17.5	23.3	25.6
1150	5,075	24.5	44.0	21.4
1300	3,200	38.5	36.2	19.8
Phosphorized Oxygen-Free, High-Conductivity Copper:				
R.T	22,400	49.3	85.5	35.7
200	18,900	53.0	86.2	34.5
300	16,400	52.0	77.0	30.2
400	16,650	48.8	88.3	29.2
500				33.7
550	14,925	43.5	78.9	
600				35.5
700	12,250	44.0	85.0	30.8
850	10,900	46.5	75.8	31.1
1000	7,750	47.3	74.4	27.4
1150	5,625	50.0	63.4	22.5
1300	4,125	70.2	98.9	19.7
Tough-Pitch Copper:				
R.T.	22,950	27.5	30.0	8.7
200	18,725	28.3	31.0	7.8
300	18,175	36.8	37.6	7.9
400	16,600	42.5	42.2	8.5
500				9.3
550	12,475	20.5	19.7	
600				8.6
700	8,840	8.3	10.3	9.3
850	6,750	5.0	9.3	8.8
1000	4,950	6.0	5.8	8.5
1150	3,500	4.8	6.2	8.1
1300	2,475	8.0	12.0	8.7

* Tensile data are averages of two tests. Impact data are averages of three tests.

** Owing to the wrinkled surfaces of the broken bars and the uneven cross sections at the fractures, the reduction of area values were impossible to measure accurately. They represent, in this case, estimated values.

amount of cracking, a fact which is reflected in the ductility curves of Fig. 6. Both the oxygen-free and the tough-pitch copper showed quite poor ductility above 500 deg. F., although the ductility of the oxygen-free copper again increased at temperatures of 1150 and 1300 deg. F. The types of fracture obtained in these two types of copper at the higher temperatures are shown in Fig. 11.

Properties of Hot-Worked Copper: Sections 4 in. square were cut from cast blocks and hot-forged to 1⅛-in. square rods. The rods were then rolled to ¾-in rounds. The forging and rolling of the bars were carried out at 1200 deg. F. Following the rolling, the bars were given a ½-hr. draw at 600 deg. F. The material for the hot-rolled bars was taken from cakes of copper cast in a manner similar to that used for the cast specimens.

Tensile specimens were machined from the bars and

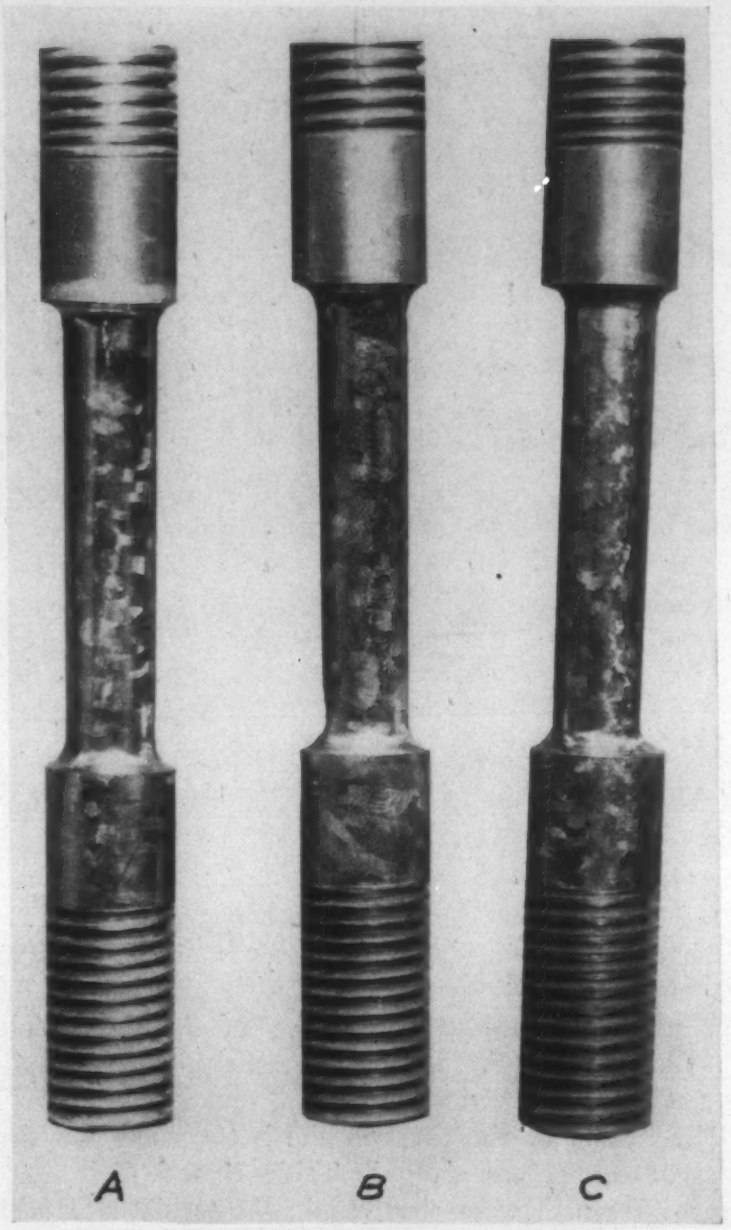
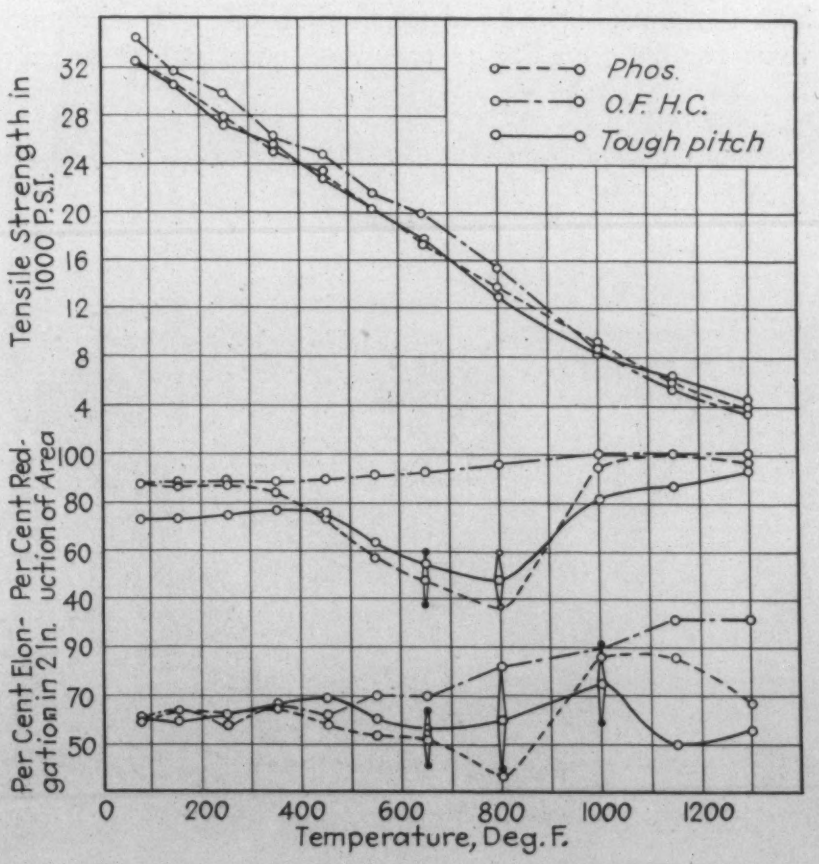


Fig. 5. Test Specimens Etched in Nitric Acid. A is O.F.H.C. Copper. B is Phosphorized Copper. C is Tough Pitch Copper.

Fig. 6. Tensile Properties of Cast Copper.



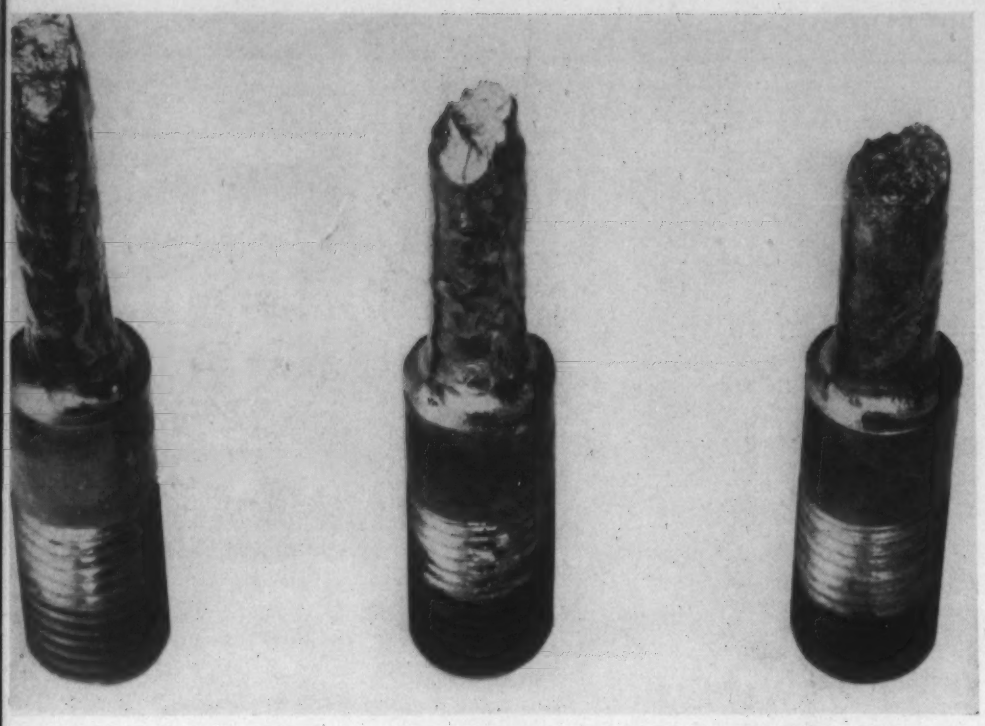


Fig. 7. Broken Test Bars from Tests at 300 Deg. F. From left to right the specimens are O.F.H.C., Phosphorized and Tough Pitch copper, respectively.

tested according to the procedure outlined for the as-cast specimens. As with the as-cast types of copper, tensile properties at a given temperature were obtained on duplicate specimens with the exception of the tests made at 150 and 350 deg. F. Insufficient stock prevented duplicate tests at these two temperatures.

The results of the tests on the hot-worked and drawn types of copper are given in Table II and Fig. 12. No great differences were observed in the tensile strengths of the hot-worked copper, as may be seen from Fig. 12. There was again a uniform falling off in strength with increase of temperature.

The reduction of area data for the hot-worked copper show that the oxygen-free copper retained its ductility over the entire temperature range. In fact a slight increase in the reduction of area and quite a perceptible increase in the elongation with increased temperature took place. In both the phosphorized and tough-pitch copper a minimum value for the reduction of area was found at 800 deg. F.

Table II. Tensile Data on Hot-Worked Copper*

Test Temp., Deg. F.	Ultimate Strength, Lbs. per sq. in.	Elongation, per cent	Red. of Area, per cent	Charpy Impact, Ft.-Lb.
Oxygen-Free High-Conductivity Copper:				
R.T.	34,400	58.8	87.1	45.5
150	31,600	63.5	87.9	40.2
250	29,800	57.5	88.2	38.7
300				37.1
350	26,300	66.0	87.9	37.4
450	24,800	62.0	89.0	36.3
550	21,600	69.3	90.7	40.2
650	19,900	69.0	91.9	45.6
800	15,400	80.8	95.3	40.8
1000	8,650	88.8	99.6	32.7
1150	5,500	100.8	99.0	26.4
1300	3,400	100.5	99.0	23.3
Phosphorized Oxygen-Free, High-Conductivity Copper:				
R.T.	32,500	59.0	87.2	45.5
150	30,750	63.0	86.0	43.7
250	27,850	62.3	86.7	39.7
300				38.9
350	25,100	64.0	83.8	36.3
450	23,250	57.5	73.3	37.4
550	20,200	53.0	56.2	39.4
650	17,400	51.8	47.6	44.1
800	13,750	36.8	35.4	41.6
1000	9,100	85.3	94.2	34.4
1150	5,900	85.3	99.2	27.7
1300	3,800	66.5	95.7	25.5
Tough-Pitch Copper:				
R.T.	32,350	60.0	72.7	34.1
150	30,500	58.5	72.3	32.0
250	27,200	61.5	74.4	31.5
300				30.2
350	25,600	65.0	76.1	30.2
450	22,850	68.5	74.6	31.1
550	20,300	59.5	62.4	32.5
650	17,750	56.0	53.8	40.6
800	13,100	59.3	46.8	39.0
1000	8,250	74.3	81.3	33.6
1150	6,350	48.8	85.3	25.7
1300	4,400	54.5	92.0	24.8

* Tensile and Impact Data are averages of two tests at each temperature with the exception of the tensile tests at 150 and 350 deg. F.

At 1000 deg. F. the ductility of these coppers increased sharply to values equal to those at room-temperature.

The elongation values for the tough-pitch and phosphorized coppers were not so consistent as one might expect. The spread in values for elongation and reduction of area at 650, 800, and 1000 deg. F. is shown in the curves. These were the only tests in which good checks on duplicate specimens were not obtained. Examination of the microstructures in several of these specimens offered no clue as to the reason for the difference in the values obtained. All of the fractures of the hot-rolled copper were either one-half or full cup. It might be mentioned that the specimens showed no evidence of cracking or pulling apart on either side of the fracture.

Fig. 8. Broken Test Bars from Tests at 550 Deg. F. From left to right the specimens are O.F.H.C., Phosphorized and Tough Pitch copper, respectively.

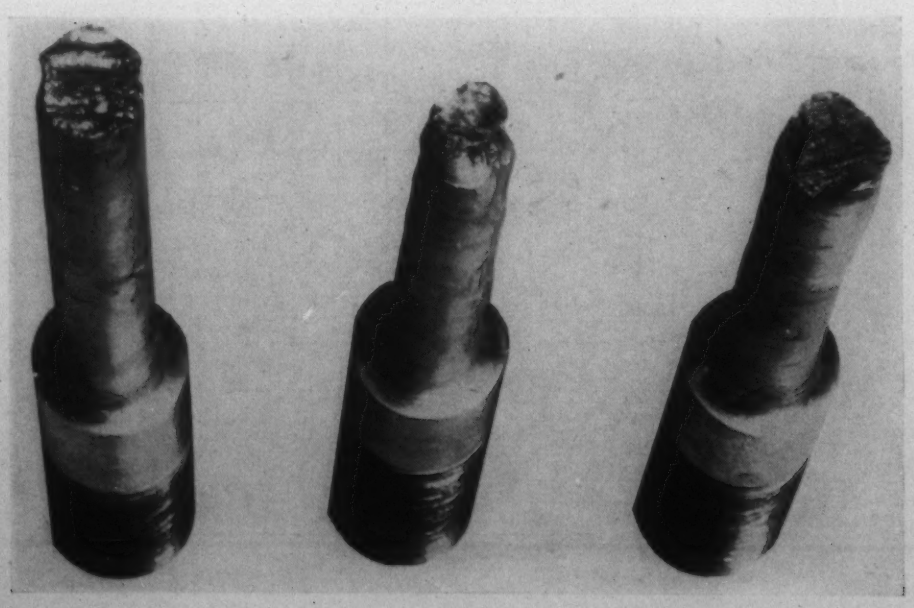


Fig. 9. Broken Test Bars from Tests at 700 Deg. F. From left to right the specimens are O.F.H.C., Phosphorized and Tough Pitch copper, respectively.

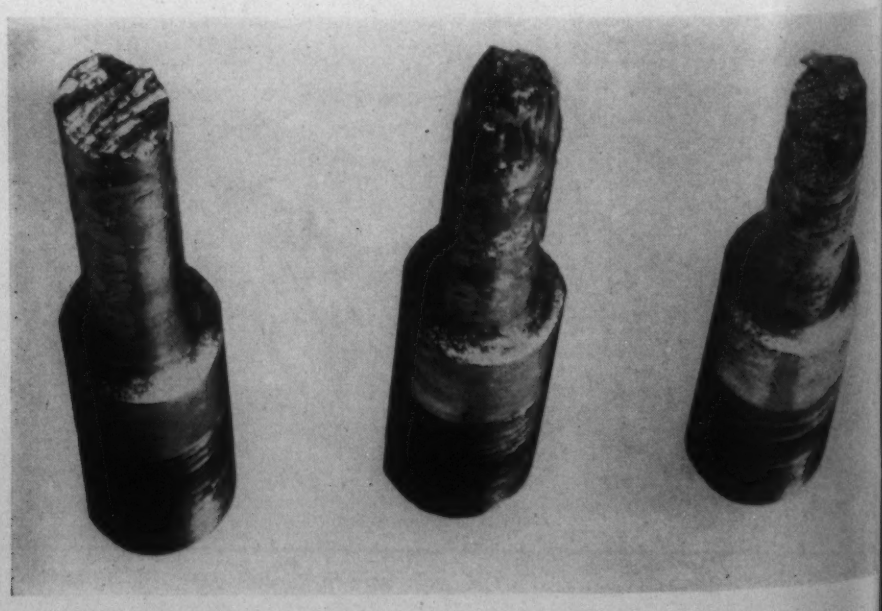


Fig. 10. Broken Test Bars from Tests at 1000 Deg. F. From left to right the specimens are O.F.H.C., Phosphorized and Tough Pitch copper, respectively.

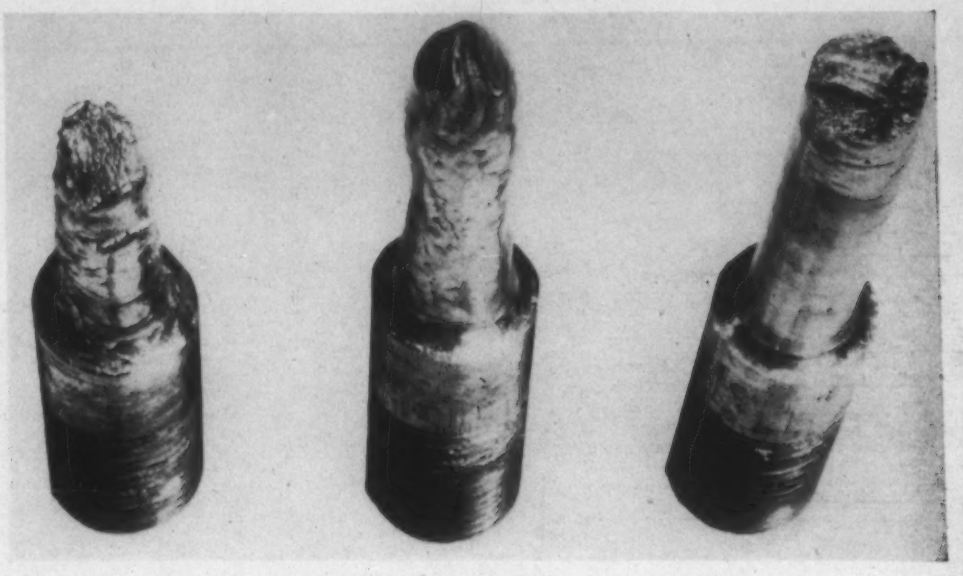


Fig. 11. Broken Test Bars from Tests at 1300 Deg. F. From left to right the specimens are O.F.H.C., Phosphorized and Tough Pitch copper, respectively.

The results of the experiments with the hot-worked and drawn copper, and particularly the ductility results as expressed by the reduction of area values, are to some extent in agreement with the work of Webster, Christie, and Pratt[3], who compared the properties of phosphorized and tough-pitch copper as affected by the annealing temperature and by cold drawing. Their results indicated outstandingly high values for the reduction of area of oxygen-free copper.

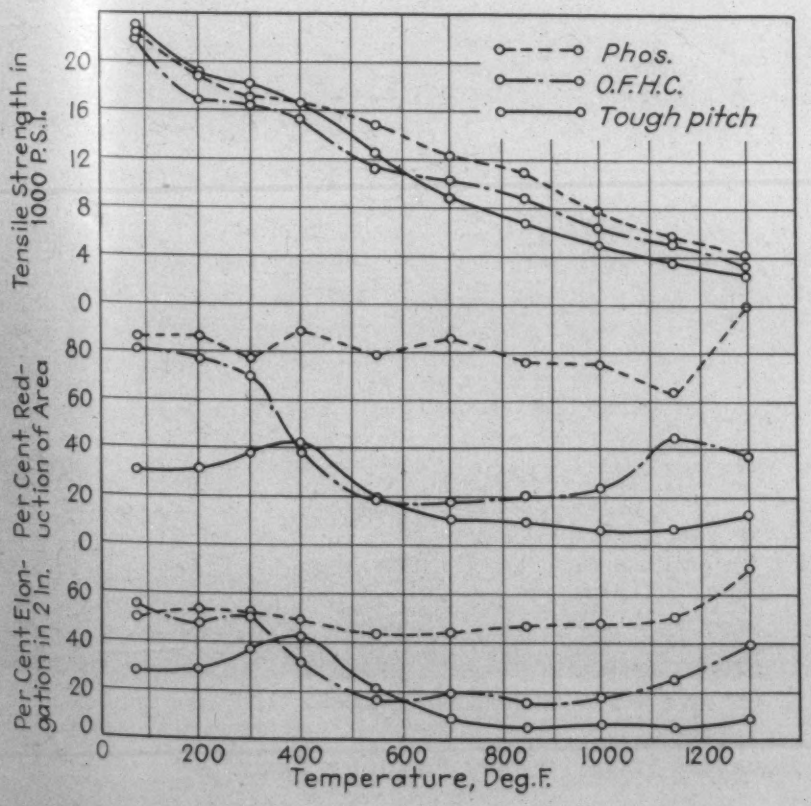
While our experiments do not show major differences in properties between the phosphorized and oxygen-free copper in the temperature range from room temperature up to 350 deg. F., the differences in reduction of area were unusually large in the range from 500 to 900 deg. F. and were favorable to the oxygen-free copper.

Impact Tests

Charpy impact tests from both the cast and the hot-worked copper were made over the same temperature range as for the tensile tests. A tubular furnace mounted so that one end was just opposite the anvil of an Amsler impact machine was used for heating the specimens. Specimens were heated to the test temperature desired and then removed rapidly, placed on the anvil of the impact machine, and broken. Calibration of a dummy specimen at the various test temperatures indicated a constant loss of a few degrees Fahrenheit in the specimen over an interval of 5 secs. The majority of the specimens were tested from 3 to 4 secs. after removal from the furnace. It is felt that the actual temperatures of the specimens broken were within 5 deg. F. of the temperature desired. Specimens were soaked at temperature for 15 mins. before breaking to insure good equalization of temperature.

The data from the impact tests are summarized in Tables I and II and Fig. 13. In the hot-rolled copper at temperatures up to about 800 deg. F. both the oxygen-free copper and the phosphorized copper have slightly higher impact strengths than the tough-pitch copper. At temperatures above 800 deg. F. the impact strengths of the three coppers

Fig. 12. Tensile Properties of Hot-Worked Copper.



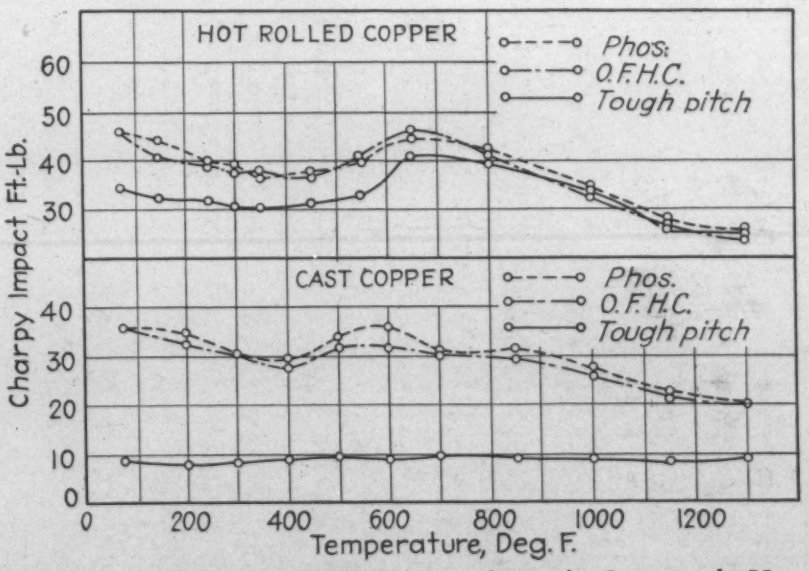
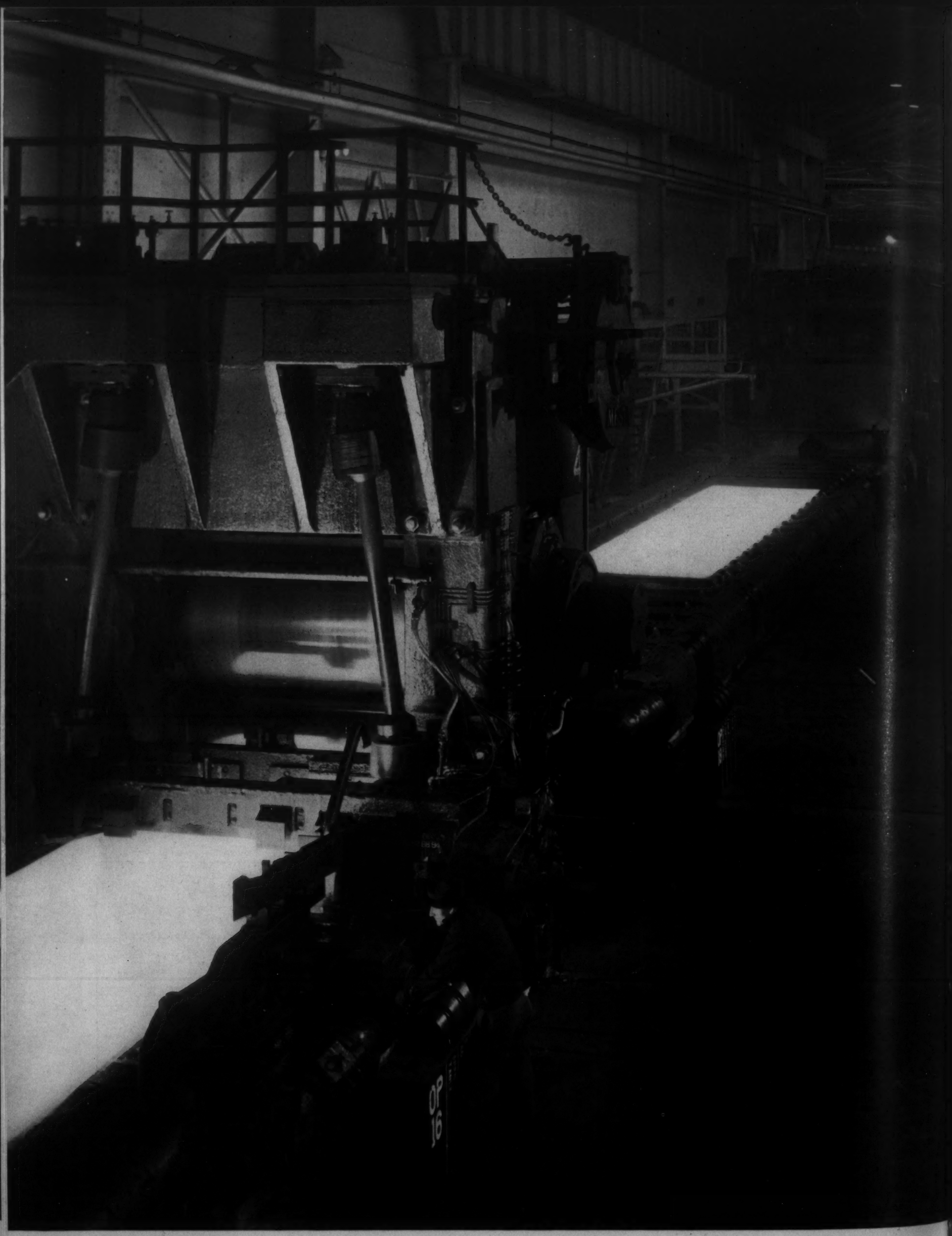


Fig. 13. Charpy Impact Properties of Cast and Hot-Worked Copper.

are about the same. The coppers showed some embrittlement in the temperature range from 250 to 450 deg. F. but recovered their impact strength at 650 deg. F., after which the impact strength fell off gradually with increase in temperature. *(Concluded on page 72)*



Courtesy: Jones & Laughlin Steel Corp.

Rolling Hot Strip: Steel Slab, After Passing Roughing Stands, Enters Finishing Train.

AN EXTENDED ABSTRACT OF A

Symposium on Powder Metallurgy

by Fred P. Peters

Assistant Editor,
METALS AND ALLOYS

The following papers were presented at the Symposium:

"Powder Metallurgy, Its Origin and Development," by Charles Hardy, of Charles Hardy, Inc., New York.

"Production and Some Testing Methods of Metal Powders," by D. O. Noel, J. D. Shaw and E. B. Gebert, all of Metals Disintegrating Co., Elizabeth, N. J.

"Types of Metal Powder Products—A Classification," by Gregory J. Comstock, of Handy and Harman, Bridgeport, Conn.

"Ductile Tantalum and Columbium," by C. W. Balke of Fansteel Metallurgical Corp., North Chicago, Ill.

"Cemented Tungsten Carbide Alloys," by W. P. Sykes of General Electric Co., Cleveland.

"Tantalum Carbide Tool Compositions," by P. M. McKenna of Vanadium Alloys Steel Co., Latrobe, Pa.

The last two papers, although of outstanding excellence, are not covered by this extended abstract because they did not feature powder technique so much as the structure, properties and testing of the finished carbides.

THE SYMPOSIUM ON POWDER METALLURGY, organized for the annual February meeting of the American Institute of Mining and Metallurgical Engineers in New York, was the first occasion, to the best of our knowledge, on which all those interested in this relatively new branch of metallurgical engineering could assemble for discussion of its status and problems. Although the Symposium itself included some unavoidable duplication of information, this at least lent emphasis to certain phases, and, in general, the collected papers offered a nicely balanced picture of powder metallurgy, from the preparation of the powders down to the applications of the molded or fabricated products. And an interesting new attitude, stressed by more than one speaker, was the general desire within the industry for more information on the "scientific" aspects—the nature of the bonding mechanism and other fundamental principles of powder manipulation.

When Should Powder Metallurgy be Used?

As pointed out by Noel, Shaw and Gebert, the application of the powder product dictates the physical properties the powder must possess and this, to a large extent, will determine what method will be adopted for manufacturing the powder. It will be helpful, therefore, to examine first the reason for using powder technique at all, in any given case.

Comstock divided the current types of metal powder products into those that employ powder technique by necessity, and those that are made from powders through choice. Correlation of his classification with Hardy's discussion of applications and possibilities shows that powder metallurgy *must* be used when:

First: The metal is too refractory to be conveniently melted and cast. Tungsten, molybdenum and tantalum, with melting points of 6100, 4700 and 5100 deg. F. respectively, are typical examples of this group. The difficulties attendant on producing such high temperatures, on finding supporting apparatus and refractories, and on overcoming losses by volatilization and oxidation are practically insuperable, and powder metallurgy has yielded product properties that are at least not inferior to those available by conventional methods.

Second: The product is required to retain, in proportion, the essential identity of each of its components. Typical of this group are the hard cemented carbides of tungsten tantalum and titanium, which manifest the hardness of the carbide constituent and yet benefit from the toughness of the binder alloy.

Third: The product must have a structure not obtainable by other methods. The porous bearing materials are characteristic of this group; their peculiar structure, and methods of predetermining controlled variation in their structure, obviously can not be developed by melting and casting technique.

Fourth: The components of the product cannot be "alloyed" conveniently, either because of excessive spread between their melting points or because they are immiscible. The electrical contact and some welding electrode materials are the most important of such products. Thus the familiar Cu-W and Ag-W composites used for contacts in electrical interrupting devices could not be commercially produced with their present properties by other than powder methods. Certain bearing and magnet composites also fall into this class.

Powder metallurgy is also used for products that can be made by other means, which, however, do not possess certain advantages offered by the newer art. Thus, powder metallurgy *may* be employed when

Fifth: The materials can be cast or forged, but with difficulty, and powder metallurgy is more convenient, or possibly cheaper. The permanent magnet alloys fall into this group.

Sixth: The usefulness of the product is increased by its purity, which would be seriously affected by the addition of deoxidizers, degasifiers or other necessary adjuncts to the melting and casting process. Comstock believes this phase of powder metallurgy application offers the greatest promise, for its many comparative advantages over casting and melting a long and varied list of products have never been explored. The possibilities in this respect are worth considering, even if all they do is to afford an easy commercial application of vacuum heating of metals, with all its obvious advantages.

Seventh: The part or article is adversely affected by cast structures. This consideration often predicates the use of powder technique in producing magnetic and thermostatic alloys.

Eighth: The article, if cast, would require excessive machining or involve considerable scrap in its manufacture. The use of powder metallurgy is particularly indicated if precious metals are involved, and the production of coins would therefore seem to be a good field for powder metallurgy.

Ninth: The product is a composite that can be made more easily from powders, through localization of composition effects; valve parts offer an excellent example of such products.

Production Technique

The foregoing are the considerations that have led to the development and application of powder metallurgy. The development of suitable manufacturing technique has been a slow, difficult process, for the experimenters had no literature or recorded experience of any kind to guide them in their early efforts. The current status of the art, its difficulties and limitations will be discussed later.

Present powder practice, Hardy pointed out, involves four stages: (1) preparation of the powder, (2) compression, (3) heat treating or sintering, and (4) final working, rolling, drawing, swaging or machining operations. The first stage was very thoroughly discussed in the paper by Noel, Shaw and Gebert.

Preparation of Metal Powders

Methods of preparing metal powders were listed by Hardy and by Noel, Shaw and Gebert. The latter authors discussed each method in considerable detail, and indicated the character of the product in each case and its suitability for various metallurgical applications. The highlights of their discussion are given in the Table.

Table of Factors in the Preparation of Powder by Different Methods

Method of Preparation	Metals so produced	Particle character	Remarks	Typical uses of Powder
Machining	All machinable metals	Irregular coarse	Somewhat costly	Dental alloys
Milling	Hard metals	Irregular fine to coarse		"Master alloys"
	Soft metals	Flake	Very flexible process	Al pigments, Cu commutator brushes
Shotting	Al, Pb, Zn	Coarse, roughly spherical	Oxidation readily occurs	Deoxidizers, gunshot, feathered Zn
Granulation	Al, Cd, Zn brass	Very coarse	Oxidation readily occurs	Thermit Al, brass for brazing
Atomizing	Several	Fine to coarse	Method varies with m.p. of metal	Most molded products (except Cu)
Condensation	Zn, Fe, Ni-carbonyls	Very fine	Highly pure	"Blue powder", Zn pigment, magnetic cores
Reduction	W, Mo, Fe, Cu, Ni, Co	Granular spherical porous	Flexible method	W filament
Chemical Precipitation	Sn, Ag, Cu, Se, Te	Very fine	Very pure	Paper coatings, Ag contacts, ruby-glass, Te-hardened Pb
Electro-deposition	Ta, Sn, Ag, Cu, Zn, Fe, Cd, Sb	All types	Low apparent density	Molded products; Ta rod, wire, sheet

Machining is usually a by-product method of powder preparation, wherein turnings, cuttings, filings, etc., from various types of machine work are salvaged. In some cases the machining operation may have the direct object of powder preparation. The method is crude and generally uneconomical, although with precious metals, where the operating cost is minor compared to material cost, it may not be impractical.

Milling involves crushing or grinding in stamp mills, ball mills and various types of attrition mills. Milling of brittle and tough metals presents no real problem, but milling of malleable metals, which tend to smear, requires special treatment. For such powders stamping or ham-

mering is usually employed; the product is flaky, and is widely used for metal paint pigments.

In *Shotting,* the molten metal is allowed to drop through a screen or small orifices, solidifying as it falls in air, and cooling in water. Metals subject to rapid oxidation in air may be "shotted" in an inert atmosphere.

Granulation is accomplished by stirring certain molten metals while they are solidifying. Metals like Al, Cd and Zn break up into granules during this "mushy" stirring, which apparently incorporates enough air to coat the particles with air or oxide and prevent coalescence.

Atomizing consists essentially of forcing a thin stream of molten metal through a small orifice and hitting the stream with steam or compressed air. Regulation of all the equipment, velocity and presure factors permits close control of powder size over a wide range. Oxidation is surprisingly small. For coarser powders and for metals that melt above 1300 deg. F. a "cross jet" method, employing right-angle impingement, is used.

Condensation of metal vapor is well illustrated in the distillation of zinc dust. Zinc oxide is vaporized in a retort and reduced to zinc vapor by CO. The metal vapor produced in the retort passes into condensers. The gas in the system should be held to a minimum of CO_2—just enough to coat the condensing zinc particles with a thin film of ZnO, which prevents coalescence and results in a very fine powder. The well-known carbonyl process for the preparation of highly pure iron and nickel powders is a special application of the condensation principle.

Reduction of compounds of the metals, particularly the oxides, chlorides and hydrides, is accomplished at temperatures below the melting point of the metal. This method is particularly well adapted to metals with extremely high melting points. With tungsten, for example, reduction is accomplished in a hydrogen atmosphere at about 2100 deg. F. This method of powder preparation is very flexible and amenable to close control of product size and properties.

Chemical Precipitation involves the deposition of one metal from a solution of its salts, by the addition of another, less noble metal.

In *Electrodeposition,* the physical character of the deposited metal may be varied by controlling all the factors familiar to electroplaters. Fine, coarse, spongy or fern-like deposits are readily produced; the metal, in all cases, must be carefully cleaned after removal from the cell. Although in some cases, the apparent density of the deposited metal is relatively low, when produced under carefully controlled conditions resulting in a high specific gravity, this type of powder behaves in practically the same manner as the porous powders made by "reduction of the oxide."

Testing of the Metal Powder

Noel, Shaw and Gebert also discussed methods of testing the metal powders. This phase of powder production is still not entirely satisfactory, and even today it is difficult to predetermine the properties of molded products through tests on molded single powders. The methods employed for testing such experimental molds, for example, depend largely on empiricism and give no definite measure of the individual characteristics of the powder responsible for the results obtained. However, quite satisfactory methods of testing the apparent density, the flow rate and the particle size distribution of batches of metal powders have been developed, and are useful for classification purposes.

The apparent density is determined simply by weighing a standard-volume container carefully filled with the powder. Flow rate is obtained by measuring the time required for a given weight or volume of the powder to flow through a standardized, funnel-shaped cup with a small orifice at the bottom.

Particle size distribution is determined by well-known screen test methods. For powders smaller than 325 mesh (0.045-0.060 mm. particle "diameter") two general types of methods are employed. The first is microscopical estimation, in which a powder sample spread on a microscope slide either is magnified and projected on a screen or is photomicrographed. This method has many drawbacks from the standpoint of accuracy and frequently entails considerable difficulty in manipulation. The other type of method is based on application of Stoke's law for falling particles; this law states, in effect, that where hindered settling is not encountered, truly spherical particles will fall through a given gas or liquid at a rate proportional to the square of their diameters.

From Powder to Product — Tantalum

Balke's outline of the production of tantalum offers a very clear illustration of the previously mentioned second, third and fourth stages of powder practice, namely compression, heat treating or sintering, and working. Because of its high melting point, susceptibility to carbon brittleness and capacity for absorbing large amounts of undesirable gases, tantalum *must* be handled by powder metallurgy, which obviates the use of melting temperatures and permits convenient vacuum treatments.

Electrolytic tantalum powder is coarser than W or Mo, which are reduced from their oxides. Inasmuch as not only the quality of the finished, fabricated product but also its production schedule depend on the character of the original powder, the chemical purity, uniformity, coarseness, etc. of the latter must be carefully controlled. Carbon must be below 0.01 per cent and Fe below 0.02 per cent. The large quantities of H_2 gas must be completely eliminated prior to the sintering operation. Particle size and distribution largely determine the subsequent heat-treating schedule, for as the coarseness of the powder increases the thermal gradient from the center to the surface of the bar increases. This establishes a definite limitation on the maximum cross section of a bar that can be satisfactorily heat treated by resistance heating, which must be employed.

Therefore, each individual lot of Ta powder is classified against grain size standards whose sintering characteristics are known. A pilot bar from each lot of powder is carried through all the steps and the finished bar is then heated by direct passage of current in vacuum furnace. The amount of current required to heat the bar to a carefully determined surface temperature is measured, and the time required to eliminate the gases originally present in the powder recorded. The experience with the pilot bar is then applied to the regular production of Ta sheet or wire from the lot of powder.

The powder is pressed hydraulically in steel dies, in which are forced one or two punches. The best that can be obtained is an approach to uniform pressing. As the pressure builds up, the powder begins to cling to the die walls, and results in a bridging action, with the result that the layers of powder adjacent to the moving punch are pressed more heavily than those farther removed. If the

pressure becomes excessive, slip cracks may be formed within the pressed piece; these cannot always be healed in subsequent operations. Bars intended for rod or wire are pressed square and weigh about 4 lbs.; bars for rolling are pressed rectangular, and weigh from 4 to 6 lbs. The pressure used is about 50 tons per sq. in. Pressed tantalum bars, even before heat treating, are surprisingly strong, and may be clamped under considerable pressure for the subsequent heat-treating operation.

The heat treating must not only effect the desired sintering, as with W or Mo, but must succeed in removing the absorbed gas characteristic of Ta. With Ta, only a small amount of shrinkage occurs during heat treatment, and subsequent heavy mechanical working replaces the shrinkage that occurs in metals made from finer powders. The sintering operation is completed by a second heat treatment, which follows a uniform schedule irrespective of the size and distribution classification of the original powder. Metallic Ta so produced is ductile at room temperature and can be rolled, drawn, spun and swaged.

The Present and Future of Powder Metallurgy

The following, taken from all the papers, is a list of products currently made from metal powders, with typical materials that are used indicated in parentheses in each case:

Addition Agents, deoxidizers, etc.
Aerated Concrete (Al-concrete)
Brake Bands (Pb composite layers)
Brazing Compounds (Brass, Ag Alloys)
Bushings and Bearings (Cu-Sn-Graphite)
Catalytic Agents (Ni, Pt)
Chemical Precipitants (Fe)
Chemical Reducers (Zn)
Clutch Facings
Coins (Precious metals)
Colored Glass (Se glass)
Commutator Segments (Pure Cu)
Condenser (electrolytic) Elements (Ta)
Corrosion-Resistant Parts (Ta, Ni-clad steel, etc.).
Cutting Tools (Carbides of W, Ta, Ti)
Decorative Applications—Lithographing (Al, brass)
Dental Alloys (precious metals)
Drawing Dies (carbides of W, Ta, Ti)
Dynamo Brushes (Cu-C)
Electric Contact Points (Cu-W, Ag-W, Ag-Ni)
Electric Resistance Elements (metal-nonmetal composites)
Grinding Wheels (metal-diamond, carbide composites)
Lamp Filaments (W)
Magnetic Cores (carbonyl Ni-Fe alloys)
Magnets (Fe-Ni-Co, Al-Ni-Co-Fe)
Master Alloys (Cu-W, Cu-Cr, Cu-Ti)
Medals (Bronze, precious metals)
Metal Paint Pigments (Al, brass, bronze flakes)
Photocell Elements (Se)
Radio Tube Parts (W, Ta, Mo, Cb)
Spark Plug Inserts (Ni cement)
Special Alloy Wire and Sheet
Spinerettes (Ta)
Spray Powder (Zn, Cd, Ni)
Thermit Al
Thermostatic Bimetals (Fe-Ni)
Warming Pad Mixture (Al-Cu)
Welding Electrodes (W-Cu)
X-ray Targets (W)

The most important applications of powder metallurgy today, according to Comstock, are for the manufacture of (1) ductile metal from materials of excessively high melting point, such as tungsten, molybdenum and tantalum, (2) hard cemented carbide tool materials, (3) porous or other special-structure bearings, and (4) electrical contact and electrode materials.

Some of the limitations of powder metallurgy that must be overcome before more widespread expansion can occur were given by Hardy. Chief among these is the difficulty in obtaining sufficient pressures for large-area work. The pressures required lie between 15 and 50 tons per sq. in., and it is easy to see that not many presses exist that could economically compress a plate, say 20 in. x 20 in. x 1/8 in., for the total pressure required would be in the neighborhood of 20,000 tons. Another difficulty is experienced in producing parts of great depth, because of the size of pressing equipment required.

One of the most serious past drawbacks to greater application of powder metallurgy, as Comstock pointed out, has been the concentration of its practical development within one industry, that of electrical products. This has been a natural and, in a narrow sense, a beneficial condition, but the application of this new art to other and broader industrial fields has been hampered by a lack of general knowledge of, and experience with it.

These difficulties clearly indicate the need for real study of the fundamental and possibly more scientific aspects of powder metallurgy. Erich Fetz, research metallurgist, Wilbur B. Driver Co., Newark, N. J., in the discussion that followed the Symposium, pointed to work already done that showed remarkable differences between recrystallization, grain growth, recovery, and diffusion effects in metals prepared conventionally on the one hand and through powder practice on the other. Probably the greatest problem of scientific interest is the nature and mechanism of the bond, and it is not unreasonable to believe that once this question alone is answered, the practical development of powder metallurgy will be greatly accelerated.

(Continued from page 67)

The impact properties of the cast copper specimens show the oxygen-free and the phosphorized coppers to have reduced impact strength values at 400 deg. F. From this temperature to 600 deg. F. the values increase after which they gradually fall off with increase in temperature. The cast, tough-pitch copper, on the other hand, shows very little change in impact strength over the entire range of temperatures. The impact strength over the entire range of the tough-pitch copper as cast, however, is quite low.

Conclusions

In the as-cast condition, the phosphorized oxygen-free copper was slightly superior to the other types of copper in tensile strength at elevated temperatures and was more ductile. After hot-working and annealing, the oxygen-free copper was uniformly ductile at all temperatures whereas the phosphorized and the tough-pitch copper showed markedly decreased ductility from 350 to 1000 deg. F.

The tensile strength of as-cast and of annealed wrought copper decreased uniformly from room temperature to 1300 deg. F.

Impact strengths of the oxygen-free and the phosphorized coppers were superior to the impact strength of tough-pitch copper. Not much difference was observed in the as-cast impact properties of the oxygen-free and the phosphorized oxygen-free types of copper.

Mechanical properties of tough-pitch copper at elevated temperatures were inferior to the properties of oxygen-free and phosphorized coppers.

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[1] Webster, W. R., J. L. Christie, and R. S. Pratt: Comparative Properties of Oxygen-Free High-Conductivity Phosphorized and Tough-Pitch Copper. American Institute of Mining and Metallurgical Engineers, Institute of Metals Division, vol. 104, 1933, pages 166-169.

A CORRELATED ABSTRACT ON

The Use of Electron Diffraction

IN STUDYING CORROSION

Part I

by I. R. Landau

University of Pennsylvania,
Philadelphia. Present address Mass. Inst. of Tech.,
Cambridge, Mass.

THE PROBLEM OF CORROSION is being viewed more and more often as the problem of surface films. An excellent survey of this trend is presented by Speller[1], who shows that the electrochemical theory of corrosion explains the formation of films at the electrodes; such films result from the reaction products of the corrosion. These films, particularly the anodic, shut off the free supply of oxygen and water, and retard the attack. They are known to be at the root of passivity and allied phenomena. Evans[2] states further that there are two kinds of films: the ultra-thin oxide films which render metals passive or relatively immune to corrosion, and which are invisible when still on the bright metal surfaces; and the thicker films, which give rise to optical interference patterns, but which are not very protective. Their formation from secondary corrosion products starts not long after the metal comes in contact with a corroding agent. The ultra-thin oxide films have a self-healing property, without which no protection is possible. This faculty of self-healing when subject to attack is of invaluable aid in corrosion resistance, and even in cases where films do not prevent corrosion, they may be important in deciding where the attack takes place.

It is true, of course, that the study of corrosion involves more than films alone, but they are of primary importance. Consequently, methods of research that will investigate the structure, composition, and formation of films are of major interest to metallurgists and engineers. Speller[1] presents the essence of the problem in this statement:

> In fact, it seems to the writer that metals having high corrosion resistance may be better developed by a scientific study of the stability and formation of surface films than by the old cut and try method of making and testing the effect of various alloying elements. Some work has already been done on the study of the electrical resistance of these films, but more knowledge of the initial rate of attack and the rate at which corrosion is retarded by the alloying of certain elements with iron should be helpful in explaining the mechanism of the resistance to corrosion.

Fig. 1. Electron Diffraction Camera, Modified Thomson-Fraser Type.

The high voltage is supplied by transformer-rectifier equipment which is not shown. Near the center of the camera are the controls for manipulating the test sample in the vacuum. The rectangular box at the top is a plate magazine holding up to 10 plates, which may be exposed successively without breaking vacuum. (Courtesy: H. R. Nelson, Battelle Memorial Institute.)

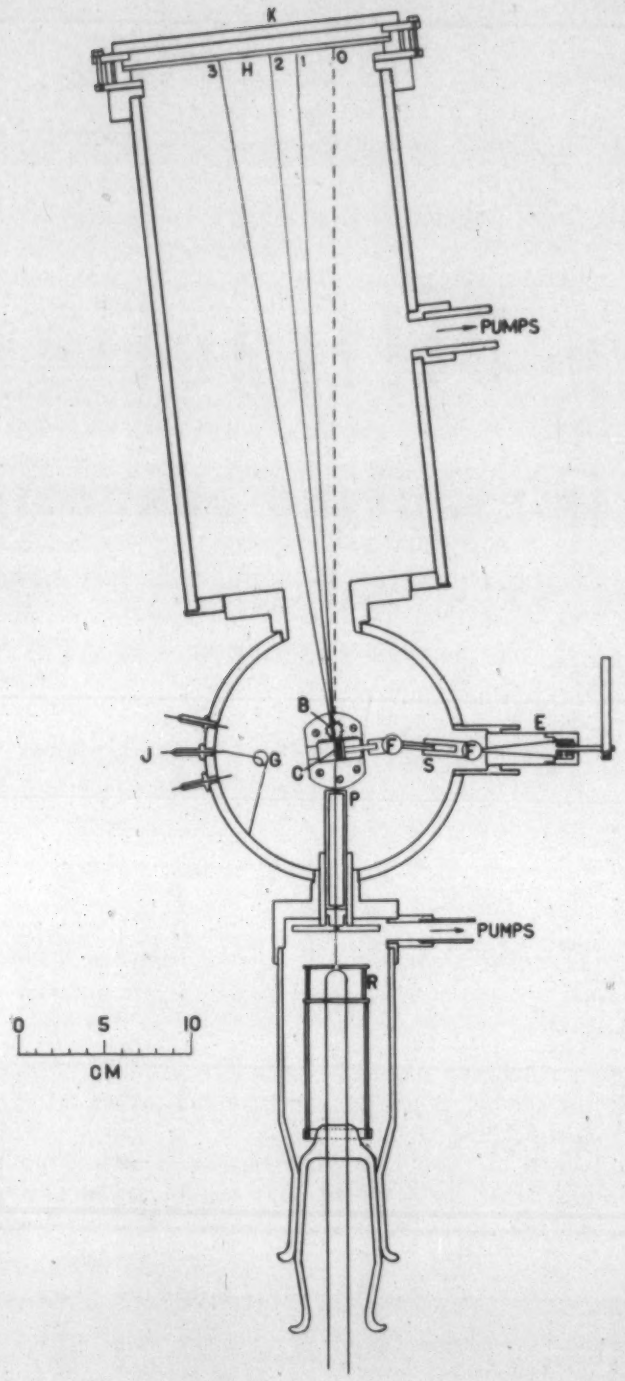


Fig. 2. Diagram of the Modified Thomson-Fraser Camera.

Electrons come from a hot filament in the box R and are accelerated by a high voltage field to the anode just above R. They then pass through a series of fine holes P and are "reflected" at grazing incidence from the surface of the sample C in various beams which strike the photographic plate H at points 1, 2, 3, etc. By means of a control at the back which actuates the pinion B, the sample may be moved out of the beam and the undeflected electrons (dotted line) permitted to locate the center of the ring pattern at O. Insulated leads J permit electric heating of the sample by means of a heater G or the formation of films in the evacuated camera by vaporization. K is a fluorescent screen on which the diffraction pattern may be observed when the plate is withdrawn to the top part of the plate magazine. (Courtesy: H. R. Nelson, Battelle Memorial Institute.)

Electron Diffraction

WITHIN the last ten years, a new method for performing such research has become available—electron diffraction. It is one of several physico-chemical procedures that have only recently been introduced into corrosion research, seemingly in fulfillment of Speller's words; they mark the initial efforts to put such investigations on a more scientific basis, and to reduce in number the long-term corrosion tests. Electron diffraction is, therefore, still a relatively untried method, which must be viewed with caution, lest the situation that followed the introduction of X-rays into metallurgical work be repeated. High hopes were held for X-rays, some enthusiasts even seeing in them the answer to all metallurgical problems; but the results have not justified such boundless optimism, although X-rays are extremely useful for certain applications. Proper moderation in the case of electron diffraction will avoid such future disappointment, particularly as there are many difficulties in its application which must be considered.

Principles of the Method

Electron diffraction is one of the basic phenomena which were predicted and interpreted by the new concepts of theoretical physics introduced in 1924. The original simple picture of the atom as a miniature solar system of electrons revolving about the nucleus gave way to the view that matter was wave-like in character. Wave-mechanics became the new physical representation of the micro-universe, and conclusive experimental proof of its validity was found in electron diffraction! Thus a subject which is of great theoretical interest is at the same time of immense practical value. Again there is a parallel with X-rays, which when first discovered were only of theoretical importance, but soon were extensively applied.

The picture of what happens when a beam of electrons strikes a thin film on a metallic surface can be related to the events that occur when light strikes the thin oil films on the wet streets after a rain. In the latter case, the light waves are broken up into their component colors by being diffracted, or bent unequally, with the resultant play of colors over the surface. By an essentially similar process, the waves of electrons that strike the film are diffracted. As an electron wave train reaches the crystals in a film, each atom of the crystal produces a wavelet which interferes with the other wavelets as in the case of the diffraction of light by a ruled grating, and an interference pattern is formed; when the crystals are all definitely oriented, a spot or arc pattern is produced [see Figs. 7, 8 and 9]; when the crystals are arranged at random, typical Debye-Scherrer patterns of concentric rings of varying diameter and brightness are obtained [see Figs. 5, 6, 10 and 12]. The patterns are characteristic of the substance under examination.

These various results were predicted by Elsasser[3], who pointed out that the confirmation of wave mechanics would be found in such diffraction experiments. Davisson and Germer[4] first obtained experimental verification of these predictions, and vindicated the theory.

Since a metallic film, or a metal, in the ordinary state, is an aggregation of small crystals, oriented at random, each like a minute diffraction grating, the use of electron diffraction can be viewed as approximately similar to that of X-rays, with this fundamental difference: the absorption of electrons is much greater than that of X-rays, and consequently, the latter penetrate much more deeply. Indeed, electrons are stopped after 10^{-5} centimeters, and therefore, the method can be used in the study of thin films on metals; under the same circumstances, X-rays would pass through into the metal beneath. Both reflection and transmission methods (the latter on isolated films) are employed, the former being more general since they are not so limited by the thickness of the film. In reflection, the electrons are projected at a small angle with the surface (5 minutes (of arc), not feet to 2 deg.), and the diffracted electrons are allowed to impinge on a photographic plate or fluorescent screen. The patterns so obtained are meas-

ured for the lattice constants, and comparison is made with the known values of expected compounds, as furnished by X-ray data. In this manner only (with rare exceptions[5]) can the identity of the compound under examination be established. The sharpness of the rings is an indication of crystal size; when the crystals are very small, diffuse rings are obtained; and indeed when highly polished metals are examined, only two very broad diffuse rings occur, showing that the crystals, if present, must be very minute.

Nature of Polished Surfaces

There has been much discussion about the character of this highly polished surface; some[6] in particular claim to have verified the existence of the Beilby layer of amorphous material. Finch[7] presents the most recent point of view of this group which feels, that although the haloes, or diffuse rings, may be due to either amorphous material or very finely crystalline substances, the fact that the layer can dissolve crystals of foreign material to saturation seems to indicate a vitreous character. Dobinski[9] also arrives at this conclusion by observing the differences in polishing in air, and away from air. Germer[8] showed that vaporized ZnS [See Figs. 4 and 5] and unpolished SiC and Cu_2O, all probably crystalline substances, gave the same halo patterns as the highly polished metals. Kirchner[10] gives a recent summary of the opposing viewpoint, and Germer[11] states that the evidence of Finch by no means settles the controversy. Both sides demonstrate that patterns obtained by reflection methods are due to transmission through thin projections on the surface, rather than actual reflection; when this surface is highly polished, these projections disappear, and the pattern loses its distinctive features. Nelson[12] corroborates this viewpoint, and states that submicroscopic roughnesses are essential if the thin films on polished metal surfaces are to be detected satisfactorily.

The general theory and technique of the electron diffraction applications are well covered in several recent publications[6, 13, 45]—the latter two giving a very recent view of the phenomenon.

Applications to Corrosion Study

THE pioneer in recognizing the value of electron diffraction, and in inspiring much of the more recent work was G. P. Thomson, whose papers[14] clearly foresaw and foreshadowed the rich field of research that was opened by Davisson and Germer's discovery. The lines along which future research employing this new tool may go are best illustrated by past experiments, *which have made little pretense at being systematic investigations into corrosion.* However, much of the significant groundwork, basic to any program of industrial research, has been laid.

Applications Requiring No Knowledge of Film Composition

First, let us consider the types of applications that will not directly require a knowledge of the chemical nature of the films.

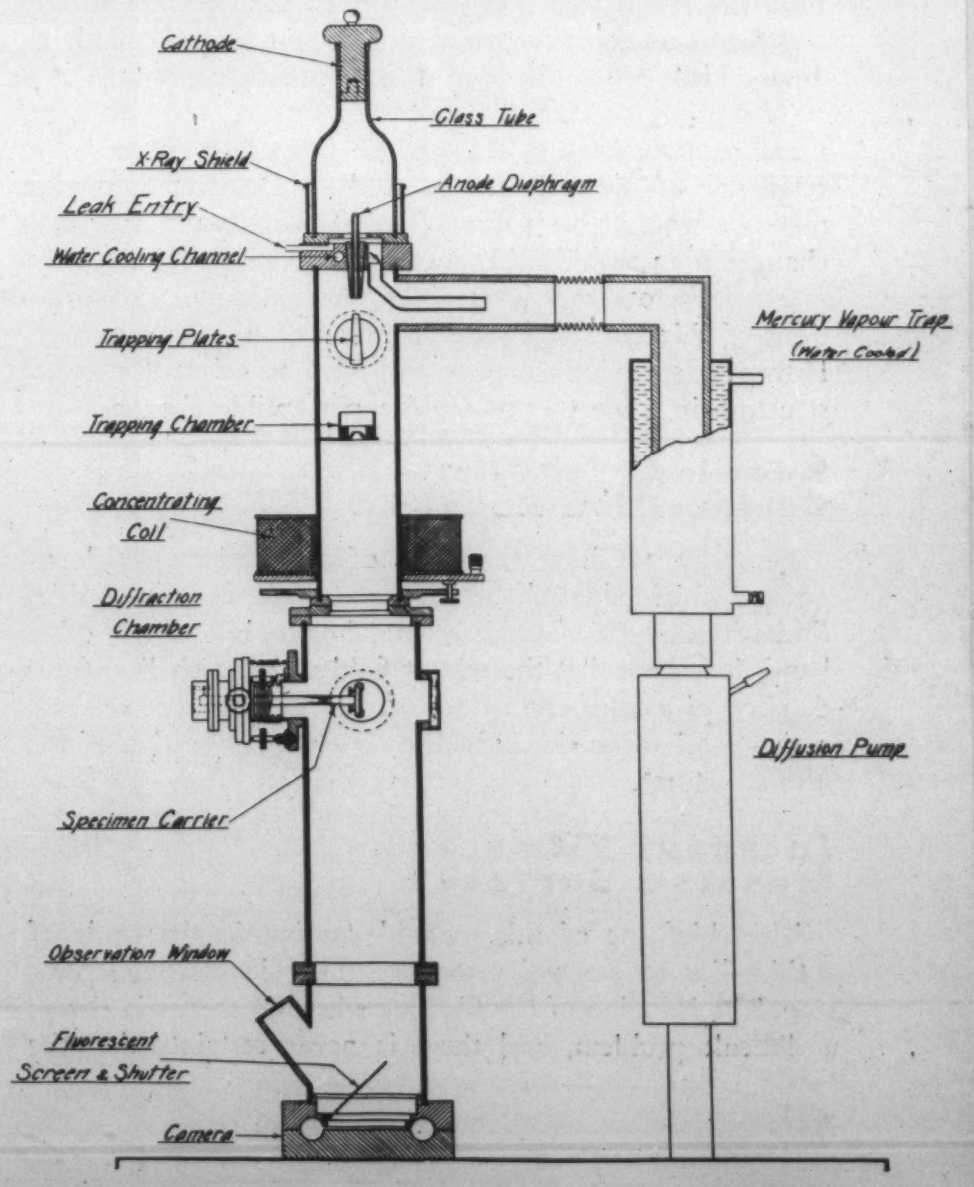
It may be possible to determine the rate and character of the film formation over various portions of the metal surface, by taking pictures at frequent intervals (only a few seconds' exposure is often enough). For example, Thum[15] states that the addition of nickel to steels considerably increases the rate of film formation. Such phenomena are of great importance, and must be studied in a fundamental fashion, by following the process of formation in terms of the physical and chemical changes involved, and the reasons for the appearance of a film at all must be sought. Local differences in attack may be caught, and reasons for them suggested, although the difficulties are great. There are several other methods that are peculiarly suited for studying the rate of film formation, such as the oscillograph and the polarograph, but these two non-diffraction methods give only a gross picture of the rates; the individual factors that enter into the corroding process can not be revealed. Electron diffraction may furnish a more detailed picture of the separate steps in the attack; such studies have been made by Nelson.[12]

The absence of a film may be detected if the pattern obtained is the same as that observed on a fresh, clean metal surface before oxidation has taken place, or if it agrees with X-ray pictures. Davisson and Germer[16] studied the surfaces of polycrystalline metals, and found that gold, tungsten, molybdenum, and cobalt gave Debye-Scherrer rings characteristic of the known structures of the metals, indicating the probable absence of an oxide film. It is of great importance in corrosion studies to know whether a film is present or not.

The lower limit of film thickness can be measured very roughly in this way; there is apparently little promise that the method will ever be able to do any better. Mongan[17]

Fig. 3. The Finch Electron Diffraction Camera.

This camera, made by Adam Hilger, Ltd., differs in a number of features from that shown in Figs. 1 and 2. The electrons are produced at the top in a gas discharge tube which must be kept at a fixed pressure by means of a controlled leak. In the center are devices for manipulating the beam, including a concentrating coil for focusing. The camera at the bottom accommodates one plate, above which is a removable fluorescent screen which may be observed through an observation window.



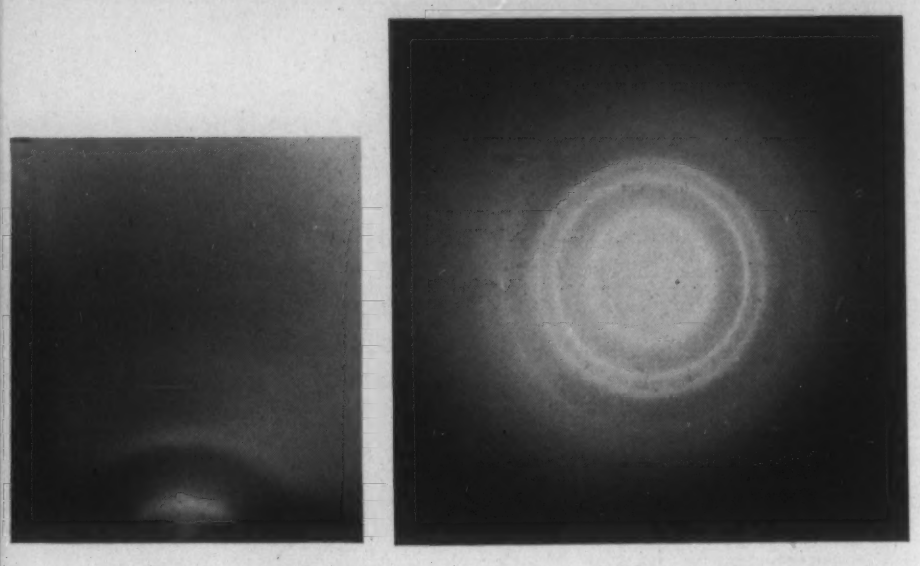


Fig. 4. Reflection. *Fig. 5. Transmission.*

Figs. 4 and 5. Electron Diffraction Patterns from a Single Film of ZnS Formed by Vacuum Vaporization. (Courtesy: L. H. Germer, Bell Telephone Laboratories.)

In Fig. 4 the electrons were reflected from the surface of the film, giving two diffuse arcs, while in Fig. 5 they were transmitted through the film, forming the sharp ring pattern of crystalline ZnS. The two diffuse arcs of Fig. 4 are similar to those obtained by reflection from polished metal surfaces and which are attributed by maany investigators to a Beilby layer of amorphous metal. Consideration of these two patterns indicates, however, that in some cases "amorphous patterns" may be obtained by reflection from thin films which are essentially crystalline. A completely satisfactory explanation of this effect has not yet been worked out.

dusted fine aluminum powder on a gauze, but was unable to observe any rings ascribable to an oxide layer; he concluded that the layer must be thinner than 10^{-5} cms., since it is known that such a film does exist. As will be shown later, his work is correct as to conclusions, but not as to details.

The effects of heat treatment and mechanical working can be traced, without knowing the composition of the film. Important light may be shed on the effect of certain treatments on corrosion resistance. X-rays are valuable here, also. Little work has been done along these lines.[19]

The effect of certain extraneous factors, such as light, pressure, temperature, etc. on the properties or corrosion resistance of the film can be studied. Electron diffraction methods would give a more fundamental insight into such changes than would other methods. Because it is often the external factors that affect corrosion resistance, investigations of this kind will suggest means of preventing attack. However, such influences would have to affect the crystal structure in some way to cause a perceptible change.

Knowledge of Film Composition Required

Secondly, we have the types of applications which require a knowledge of the film structures. Here, the chief limitations of the method are in evidence, but, on the other hand, it is here that the widest field of research lies, for a detailed picture of the nature of the attack and of the corrosion mechanism depends directly on a knowledge of the film structures.

Integral Films on Massive Surfaces

The chief use of this method consists in the study of a thin film on a massive metal surface, in cases of corrosion. The isolation of the films by whatever means is always a difficult problem, and there is never certainty that the nature of the film is not altered in the process. This may be particularly true of the orientation of the molecules. Jenkins[18] confirmed this contention when he studied the films on molten lead, zinc, bismuth, tin, etc., first by reflection, and then removed them with a nickel gauze and examined them by transmission. The patterns obtained in the latter case showed that the isolated films were of the same chemical composition, but of a *different, random orientation.* That this is of great significance is readily apparent, particularly in view of the known influence of orientation on corrosion.[19] Smith[20] also raises the salient point that electrolytic removal of the films may cause a change in the structure of the oxides (this may have been especially true of copper), and suggests the possibility of further research in this field.

Reflection vs. Transmission Methods

On the other hand, in many cases, the patterns by reflection methods agree with those obtained by transmission. Davisson and Germer[16] found NiO on nickel by reflection; Darbyshire[21] and Preston[22] investigated the same metal film by both reflection and transmission and observed identical structures. Darbyshire describes a method originally due to Evans of isolating films electrolytically. The metal in question is cleaned; one piece is heated and made the anode, while the cathode is unoxidized metal. The oxide skin is soon found to hang loose; it can be caught for examination by transmission, or for other types of analysis.

In still other cases, the reflection method may be unsatisfactory to a certain extent; this is exemplified by aluminum, which has been extensively studied. Preston and Bircumshaw[23] found that, by reflection from the surface, two broad, diffuse rings resulted. They then treated the same metal with HCl gas at about 480 deg. F., to dissolve away the base metal, leaving the film; on examination by transmission, it gave the same halo pattern—thus confirming the conclusion that it was amorphous. Above 1250 deg. F., however, crystallization begins slowly, and the film becomes the cubic γ-Al_2O_3. Mongan[17] had assumed a crystalline Al_2O_3 film when he estimated its thickness; his assumption was apparently wrong, but his estimate was probably correct, since gravimetric determination by Preston and Bircumshaw confirmed the conclusion that the film was less than 10^{-6} cms. thick.

These same authors also isolated the films from molten aluminum by withdrawing a loop of wire from the surface, and examining the layer by transmission. At these temperatures, the γ-Al_2O_3 occurred; at about 1825 deg. F., the film could not be identified. Belwe[24] prepared alumina films by electrolytic oxidation, and upon examination found the γ-Al_2O_3 in a finely crystalline form; the film resulting from flame oxidation of the metal was the same compound but of the *usual coarseness.* These results are directly comparable to those of Preston and Bircumshaw, explained above in terms of temperature effects.

Beeching[25] looked at the question from a still different point of view. He evaporated aluminum, copper, and chromium films in the evacuated camera, and studied the films so obtained; the aluminum oxide that he found was related to γ-Al_2O_3; chromium gave similar patterns, the oxygen apparently coming from the glass. Heating up to 500 deg. F. caused no changes. Steinheil[26] however, in an earlier paper, also investigated the aluminum surface; he

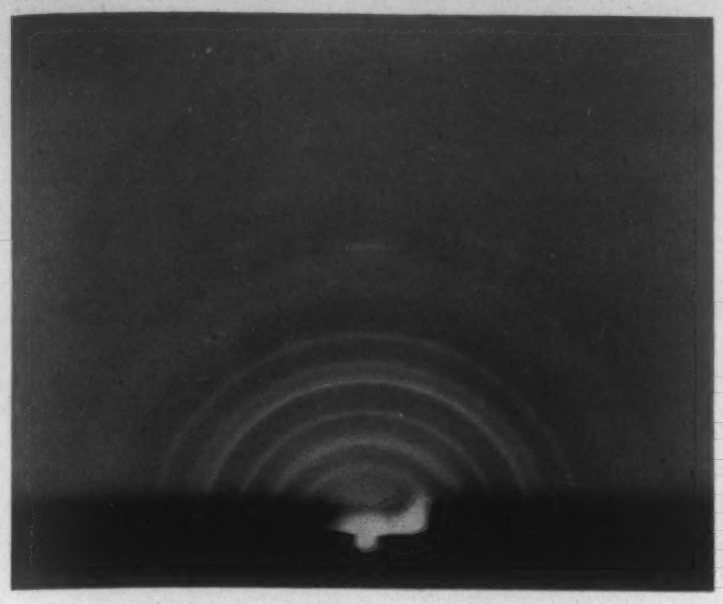


Fig. 6. Electrodeposited Iron Surface Before Cleaning.

Fig. 7. Same Surface After Cleaning.

When iron is deposited electrolytically, washed and dried, the surface may be covered with an invisible film of rust. Fig. 6 shows the electron diffraction pattern from such a surface. The rings are due to γ-FeOOH, the principal constituent of ordinary rust, and they nearly obscure the pattern of the underlying iron. After this sample was cathodically cleaned in NaCN solution, the pattern of Fig. 7 was obtained. The spot pattern proves that the electrodeposited iron crystals are oriented with (111) planes parallel to the surface of the sample. The rings of the rust pattern are still present after the cleaning treatment, although they are much fainter. The fact that the corrosion pattern consists of continuous rings on the highly oriented from pattern shows that rust crystals do not have a definite orientation relationship with the underlying iron, as is the case with the primary air-formed oxide. (See Figs. 8 and 9.) (Courtesy: H. R. Nelson, Battelle Memorial Institute.)

isolated the film by dissolving metal foil in HCl, and concluded that a hitherto unknown structure of Al_2O_3, ϵ-Al_2O_3, occurred at room temperature. Heated aluminum gave γ-Al_2O_3 by transmission, in agreement with the others. In another earlier paper, Darbyshire and Cooper[27] studied the oxide on the molten metals—antimony, copper, tellurium, calcium, cadmium, magnesium, aluminum, bismuth, and tin. The first four gave no films; they found Al_2O_3, MgO, and CdO on the next three, but there were many peculiarities, especially in the intensities of the rings, and they felt that newer theories were needed.

These researches illustrate some of the difficulties encountered in examining the surface of even so common a substance as aluminum; many lines of attack were used, and definite conclusions were not drawn until very recently. It took a long time to recognize that the film at room temperatures was amorphous. Much more work will the γ-Al_2O_3 in a *finely crystalline form;* the film resulting have to be done before reflection methods can be considered entirely reliable.

A good example of the successful application of reflection to metal analysis is afforded by the important paper of Miyake.[28] On pure copper, bronze, manganese bronze, copper-magnesium, and copper alloys, he found a Cu_2O film up to 390 deg. F., but a CuO film at higher temperatures; however, an intermediate CuO film, which gives an extra ring, is formed at 570 to 1020 deg. F. The films formed on aluminum bronzes containing more than 3 per cent aluminum depend on the method of heating. Thus, in an electric furnace, the alloy behaves like pure copper, and acquires a black coat of CuO, but long heating in a gas flame causes no change in color although electron diffraction shows the surface is covered with a thin film of cubic γ-Al_2O_3, which protects the surface from further oxidation.

The reason for this is the limited oxygen supply in the gas flame; since aluminum has a greater affinity for oxygen than copper, γ-Al_2O_3 formation is favored, despite the low aluminum content. He found also that brass (30 per cent zinc) is covered with ZnO at 1290 deg. F. in the electric furnace, but CuO is found in the gas flame. Beryllium bronze (up to 2 per cent beryllium) resists oxidation, due to formation of BeO.

In a second paper[29] Miyake studied iron alloys and steel. A γ-Fe_2O_3 film was observed on iron above 480 deg. F., and Fe_3O_4 at lower temperatures; however, Fe_3O_4 was also detected in the layer underneath the Fe_2O_3. On iron-aluminum and iron-nickel alloys, only γ-Fe_2O_3 was found, but on stainless steel, $FeCrO_4$ coexisting with Cr_2O_3, or a solid solution of Cr_2O_3-Fe_2O_3 was observed. Pure $NiCr_2O_4$ forms on nickel-chromium resistance alloys; a CuO film occurs on copper-nickel alloys, but an underlying NiO film may be present. It is readily apparent that investigations of this kind can do much to improve alloy research, by making plain the constituents responsible for corrosion resistance, permitting in this way the elimination of rule-of-thumb additions.

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(To be concluded)

Letters to the Editor

Hardening with the Acetylene Torch

To the Editor: In "Crankshafts and other Parts Surface Hardened by Inductive Heat" by Edwin F. Cone, published in your January, 1938, issue, the statement is made that "the use of the acetylene torch for this purpose is a more modern process."

Recent discussion of surface hardening with the acetylene torch has not included a bibliography of the subject. A search of the literature would have disclosed the Vickers-Sumter process which was in use in England before 1914. This process was, I believe, used for tooth by tooth surface hardening of automobile rear axle bevel gears and other purposes.

I, likewise, have not looked up the literature and am quoting from memory. My remembrance of the process is kept alive by the fact that in 1914 I was associated with an aircraft engine project using roller bearing connecting rod big ends. In this engine the rollers ran directly on the crankpins which were locally hardened by the Vickers-Sumter process, the steel used for the shaft being a special grade produced by Vickers, Ltd., especially for use with their process.

Since I have conducted no literature search my spelling of Mr. Sumter's name may be in error.

S. D. HERON.

Ethyl Gasoline Corporation,
Research Laboratories, Detroit.

Inoculation by Ni, Si or Al?

To the Editor:

Inoculation

According to Everest (page MA 12 R 2) a method of manufacture of high test involves "inoculation by Ni," but we note that about ½ per cent Si as well as 1 per cent Ni is added. Which is the inoculation, the Ni or the Si?—H.W.G. (From "Highlights" in January issue.)

Which is the inoculation?

If I were asked that question, the answer would probably be that neither nickel nor silicon is the inoculation agent but the small amount of aluminum contained in normal ferrosilicon as an impurity. At least the special low aluminum grades are much less efficient when used for ladle inoculation of gray iron.

We of the foundry industry are inclined to be careless in drawing our conclusions. Most of us have noticed that a ladle addition of ferrosilicon has a great deal of graphitizing effect as compared to the same amount of silicon added in the cupola or furnace. Instead of investigating to find what we are adding beside silicon, we merely formulate a theory that late addition of silicon is more effective than the same addition to the furnace and let it go at that.

It is very probable that the addition of a minute quantity of aluminum results in the formation of a cloud of alumina inclusions which act as nuclei for graphitization. Holding at temperature for any length of time or slag treatment such as is usual in the cupola or melting furnace will tend to eliminate such inclusions and in that way destroy the inoculation effect.

METALS AND ALLOYS is to be commended on the article in the January issue—"Notes on the Graphitization of Gray Cast Iron." The idea of graphitization from the melt is generally considered unorthodox but it does seem to explain some of the structures commonly observed in gray iron. At least such articles serve to focus attention on a subject which deserves a great deal more investigation.

Yours very truly,

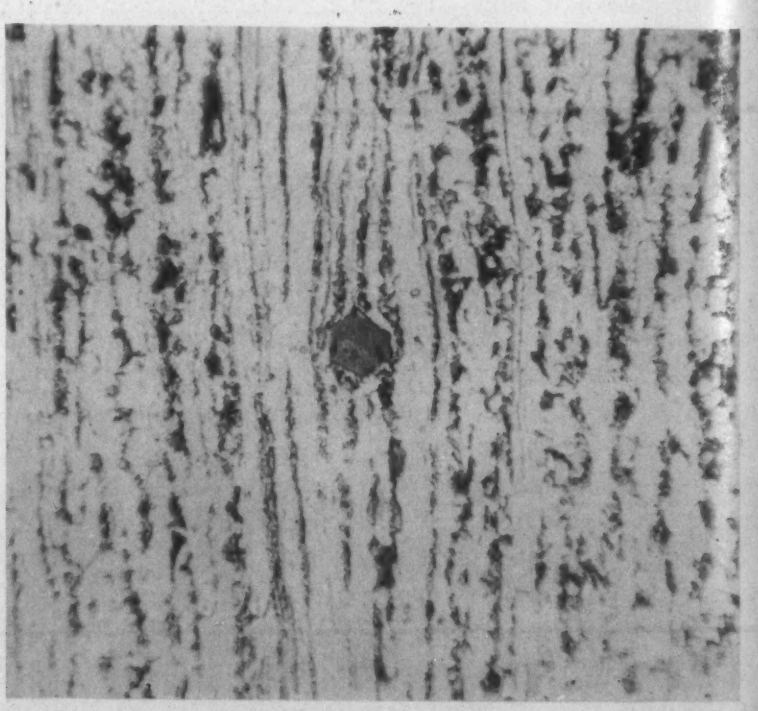
R. A. CLARK,
Metallurgist.

Lakey Foundry & Machine Co.,
Muskegon, Mich.

Sulphide Inclusions in Iron and Steel

To the Editor: METALS AND ALLOYS has brought to our attention some remarkable photographs of sulphide inclusions in cast iron and steel (O. W. Ellis, METALS AND ALLOYS, August, 1937, p. 221; and C. E. Sims, December, 1937, p. 362).

The accompanying microphotograph (X 500) might also prove of interest in this connection. It was obtained from a ⅛-in. plate of mild steel. The inclusion has a distinct hexagonal shape. One would call it a "manganese sulphide" inclusion, although it is certain not to represent pure manganese sulphide, which crystallizes in the regular system and could not show a section



of the type seen. Iron sulphide crystallizes in the hexagonal system, and possibly the inclusion in the present case is a mixed sulphide with an appreciable amount of iron sulphide. Obviously, the inclusion has formed prior to the metal passing the solidus line (1490° C.). The iron sulphide-manganese sulphide equilibrium system gives for 1490 deg. C. a manganese-sulphide percentage of 64 per cent. According to this reasoning, one would suspect an iron sulphide content of up to 36 per cent.

However that may be, the photograph would seem to indicate a feature of great interest: The hardness of the inclusion, even up to fairly high temperatures. The etched sample shows distinctly that, during the process of rolling, the pearlite, once formed, has flown around the inclusion, this in itself not having suffered any change of shape.

Dr. O. A. JESCHE.

Metallographic Research Laboratory,
Randfontein Estates, G. M. Co., (W) Ltd.,
Randfontein, South Africa.